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A manufacturing perspective on graphene dispersions

David W. Johnson, Ben P. Dobson, Karl S. Coleman *

Department of Chemistry, Durham University, South Road, Durham DH1 3LE, United Kingdom

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ABSTRACT

Harnessing the exceptional physical properties of graphene often requires its dispersion into aqueous or organic media. Dispersion must be achieved at a concentration and stability appropriate to the final application. However, the strong interaction between graphene sheets means it disperses poorly in all but a few high boiling organic solvents. This review presents an overview of graphene dispersion applications and a discussion of dispersion strategies: in particular the effect of shear, solvent and chemical modification on the dispersion of graphene (including graphene oxide and reduced graphene oxide). These techniques are discussed in the context of manufacturing and commercialisation.

1. Introduction

Graphene is a true wonder material and has the potential to generate disruptive technologies. Since it was isolated in 2004 [1] a wide range of impressive properties have been reported for graphene including the following: high electron mobilities of over 200,000 $cm^2 V^{-1}s^{-1}$ at electron densities of ~2×10^{11} cm^{-2} [2], high thermal conductivity of ~5×10^3 $W m^{-1} K^{-1}$ [3], impermeability to gasses despite being one atom thick [4], ballistic transport of electrons [5,6], absorption of 2% of the light passing through it [7], and being "the strongest material ever measured" [8] with a Young's modulus of TPa. The fact that all of these properties are found within a single material has stimulated great interest in graphene. In spite of this, it is still only at the early stages of commercial development as a number of challenges need to be addressed. The first of these has been a lack of scalable synthetic routes to produce graphene in the quantities required for industrial applications. However, a number of methods for scalable graphene synthesis are now emerging [9]. The second problem relates to the difficulties in processing graphene, in particular graphene's poor colloidal stability in most common solvents [10].

For a graphene dispersion to be useful, essential criteria must be met: the graphene must disperse at a useful concentration, in a solvent appropriate to the application, and remain dispersed over a reasonable period of time. Current strategies to solve these challenges are the subject of this review.

2. What makes a good dispersion?

The parameters for creating a good dispersion are well established in the field of colloid science [11]. The free energy of any colloidal system is determined by both the interfacial area and tension. The theoretical surface area of monolayer graphene is ~2590 $m^2 g^{-1}$ [12]; consequently there are a limited range of conditions under which it can be dispersed typically involving sonication and polar aprotic solvents [13].

Maintaining a dispersion requires an energy barrier to aggregation be introduced. This can be achieved by either electrostatic or steric repulsion [14]. If the energy barrier is sufficiently high then Brownian

Abbreviations: ATRP, atom-transfer radical-polymerisation; Brij700, polyoxyethylene (100) octadecyl ether; CHAPS, 3-((3-cholamidopropyl)dimethylammonium)-1-propanesulfonate; DBDM, n-dodecyl β-D-maltoside; DCC, N,N′-dicyclohexylcarbodiimide; DLS, dynamic light scattering; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; DNA, deoxyribonucleic acid; DOC, sodium deoxycholate; EDC, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; EDTA, ethylenediaminetetraacetic acid; EDTA–silane, N-(trimethoxysilylpropyl) ethylenediamine triacetic acid; G, pristine graphene; GBL, γ-butyrolactone; GNP, graphite nanoparticle; GO, graphene oxide; GPTMS, 3-glycidoxypropyltrimethoxy silane; GrO, graphite oxide; HATU, 1-[bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate; IPA, isopropyl alcohol; NMP, N-methyl-2-pyrrolidone; P-123, Pluronic® P-123; PAH, polyaromatic hydrocarbons; PBA, 1-pyrenebutyric acid; PC, propylene carbonate; PEDOT, poly(3,4-ethylenedioxythiophene); PEI, poly(ethylenimine); PEO, poly(ethylene oxide); POM, polyoxometalate clusters; PPO, poly(propylene oxide); PSA, 1-pyrenesulfonic acid sodium salt; PSS, polystyrene sulfonate; PVA, poly(vinyl alcohol); PVAc, poly(vinyl acetate); PVP, poly(vinylpyrrolidone); rGO, reduced graphene oxide; SDS, sodium dodecyl sulfate; SDBS, sodium dodecylbenzenesulfonate; SLS, static light scattering; TDOC, sodium taurodeoxycholate hydrate; THF, tetrahydrofuran; TMU, tetramethylurea; TRIS, tris(hydroxymethyl) aminomethane; UV, ultra-violet.

* Corresponding author. Tel.: +44 1913342116.
E-mail address: k.s.coleman@durham.ac.uk (K.S. Coleman).

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motion will maintain the dispersion [11]. This can be achieved by solvent selection [10,15,16], or by the modification of graphene either covalently or non-covalently [17].

From a manufacturing viewpoint the pressing challenges include the following: increasing the range of dispersing solvents to include those which are volatile and less toxic e.g. alcohols and water; improving dispersion stability as a function of concentration, time, temperature, and ionic strength; and more scalable routes to dispersion e.g. high shear mixing as opposed to sonication. In addition to these there are a series of second tier challenges which include the following: accurate characterisation, safe handling, and post-processing. The final, but crucial challenge, is dispersions must be achieved in a cost effective way.

2.1. Types of graphene used in dispersions

"Graphene" is often used to refer to a family of materials including the following: pristine graphene (G), graphene oxide (GO), and reduced graphene oxide (rGO). These materials can be further subdivided by the method of production, in particular G. However, nomenclature for graphene and its derivatives is varied with some terms being used to describe a range of materials. A formal nomenclature has been proposed by Bianco et al. but is not universally used and so care must be taken in interpreting results [18].

In the context of dispersion G is nearly always produced by solvent or surfactant assisted graphite exfoliation [13,19,20], although exceptions exist [21]. G has properties closest to those of defect free "pristine" graphene [19]; the dispersion is a mix of single to multi-layer graphene and graphite although these components can be separated [22]. GO is produced by the exfoliation of graphite oxide (GrO), which is easily achieved in water [23], however it is a very defective material with markedly different properties from G [24]. Finally, rGO is produced by the reduction of GO, generally by either chemical, or thermal methods [25,26]. The removal of the majority of oxygen functionalities from GO means rGO's properties are close to those of G, but the material remains defective [26,27]. A further related material used in dispersions are graphite nanoplatelets (GNPs) which are nanosized graphite flakes [28].

Unfortunately the dispersibility of graphene and its derivatives is almost inversely proportional to its physical properties. As a simple guide, dispersibility follows the trend GO > rGO > G. Chemical functionalisation of these materials can improve dispersibility but can also increase their defectiveness and have a negative impact on properties [29,30].

As a result there is often a compromise between the ability to process the material and its resultant physical properties. Selecting the correct graphene, and, where applicable, the correct functionalisation method requires consideration be given to the end application: a subject which has been reviewed elsewhere [9].

2.2. Dispersion of graphene

Several solvents have been identified as being particularly good at dispersing graphene in particular: NMP, DMSO and DMF [15]. Ionic liquids (ILs) have shown some promising results, however as they are not widely used in industry they are beyond the scope of this review and interested readers are directed to a recent review [31]. Generally research into G dispersion is combined with its exfoliation from graphite; while exfoliation and dispersion are distinct phenomena they are related.

Solvent interactions with graphene have been rationalised in terms of both surface energies and Hansen solubility parameters [15,19]. However, as highlighted in a recent review, there are problems with both these approaches [32]. Despite this, work in this area has produced useful results in identifying and predicting good G solvents. Recent molecular dynamics simulations support what has been found experimentally, namely that:

$$\mathrm{NMP} \approx \mathrm{DMSO} > \mathrm{DMF} > \mathrm{GBL} > \mathrm{H_2O}$$

for G dispersion [33]. The mechanism of this dispersion is attributed to a layer of confined solvent near the G surface which prevents aggregation of G sheets *via* sterics.

The dispersion of G into solvents is most commonly achieved by sonication, which creates shear stresses and cavitation in the solvent [34]. This has the effect of breaking apart graphite and exfoliating the sheets into individual G flakes. The dispersion concentration is known to be linked to both the sonication time and power (Fig. 1) [16]. By far the most widely used solvent for dispersing graphene is NMP, where sonication of graphite can yield stable G dispersions in the range of 0.01–2 mg ml^{-1} [16,19]. G, which has been isolated from its parent graphite can be redispersed to concentrations of up to 63 mg ml^{-1} (falling to 33 mg ml^{-1} over 200 h) [16].

The extreme conditions of sonication even allows for the dispersion of G in to poor, low boiling point solvents including the following: acetone, chloroform, IPA, and cyclohexanone although a 48 h sonication time is required [35]. However, long sonication times are generally undesirable as it can reduce sheet size and introduces defects which undermine graphene's properties [35–37].

Alternatives to sonication exist, recently both Liu et al. and Paton et al. used a high shear mixer to produce G dispersion in NMP of 0.27 mg ml^{-1} and 0.07 mg ml^{-1} respectively [38,39]. Paton et al. noted that non-turbulent local shear rates of $>10\times10^4\ s^{-1}$ were necessary for exfoliation. From an industrial perspective high shear mixing is a promising technique as it is a more mature technology than ultrasonication.

It has also been demonstrated that ball milling with organic solvents can be used to disperse graphene [40]. Tested solvents included NMP, TMU, DMF, THF, acetone, ethanol, and formamide with concentrations of 88, 88, 97, 76, 66, 10.32 and 3.67 μg ml^{-1} found respectively.

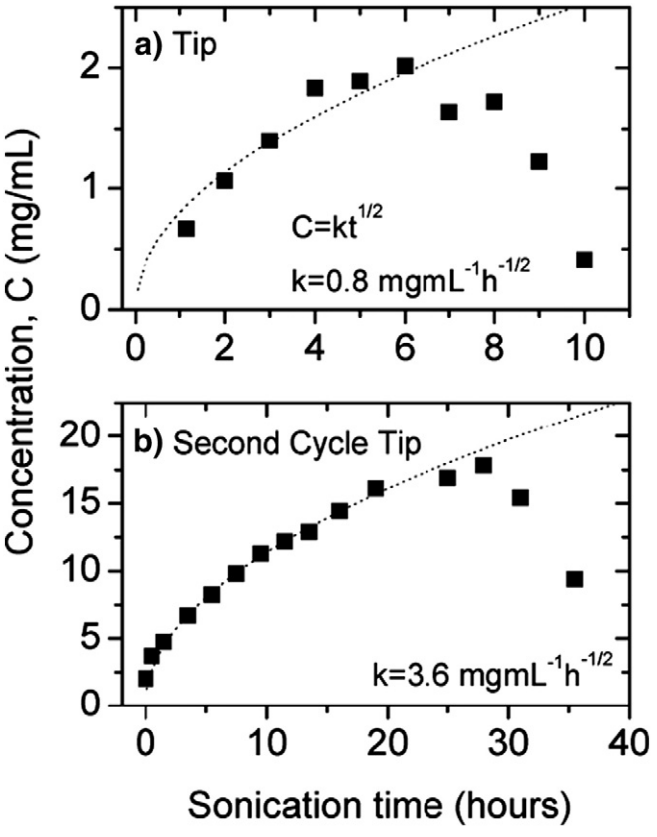

Fig. 1. (a) Exfoliated graphene concentration as a function of sonication time of graphite in NMP. (b) Concentration of graphene redispersed after isolation from graphite. Note that on isolating the graphene from graphite that the total concentration of graphene dispersion increases dramatically.
Reprinted with permission from Porwal et al. [16].

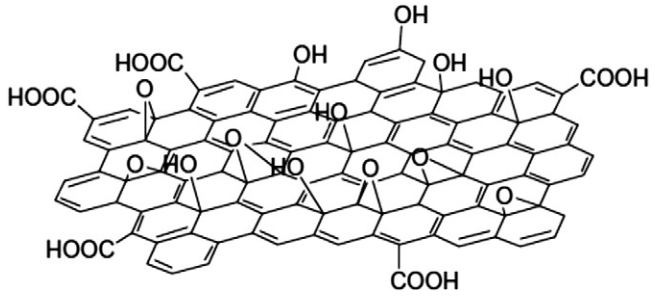

Fig. 2. Proposed structure of GO comprising epoxy, hydroxyl and acid groups. Reproduced from [49] with permission from the Royal Society of Chemistry.

2.3. Dispersion of graphene oxide

A widely used route to graphene dispersions is *via* GO, produced by the oxidation of graphite to GrO [41–43]; the oxygen species allow the GrO to be easily exfoliated with respect to graphite [44]. The resulting GO is highly functionalised, with groups including carboxylic acids and epoxides (Fig. 2) [45–49], affording a carbon to oxygen ratio of between 4:1 and 2:1 [50]. As a result it is also highly defective to the extent that it is electrically insulating.

The functional groups allow GO to be dispersed in a range of solvents (Fig. 3) [27,51], polar aprotics such as DMF and NMP have been shown to be able to spontaneously exfoliate GrO forming liquid crystal phases [44]. Polar protics, including ethanol, are unable to spontaneously exfoliate GrO, but can disperse GO sheets by solvent exchange from water [44]. As with G, intense sonication widens the number of solvents which can disperse and exfoliate GO (Table 1) [27].

However, by far the most common solvent for GrO exfoliation and dispersion is water [52,53]. In water GrO can be exfoliated either by sonication [16,54], or even gentle shaking [55]; as a result control over lateral sheet sizes can be achieved [56]. GO concentrations of up to 0.025 wt.% are easily achieved after which nematic liquid crystalline phases form [57], although the nematic transition appears to be dependent on sheet size [58].

The GO dispersion is maintained by the electrostatic repulsion of carboxylate groups present, with typical zeta potentials of −64 mV in water [57]. Protonation of the carboxylate groups results in the reversible agglomeration of GO [59,60]. In addition it is possible to screen the charge between carboxylate groups with salts triggering aggregation [61]. As the carboxylate groups are located at the sheet edge smaller sheets are more charged than larger, consequently control of pH [62,63], or ionic strength [61], offers an alternative to centrifugation as a means of separating small from large GO sheets [57,64]. The associated GO morphology changes and folding of GO in water have been reviewed elsewhere [65].

Table 1
The solubility of GO and rGO in a range of solvents by bath sonication. Reprinted (adapted) from Konios et al., with permission from Elsevier [27].

Solvent	GO solubility/μg ml^{-1}	rGO solubility/μg ml^{-1}
De-ionised water	6.6	4.74
Acetone	0.8	0.9
Methanol	0.16	0.52
Ethanol	0.25	0.91
Propan-2-ol	1.82	1.2
Ethylene glycol	5.5	4.9
Tetrahydrofuran	2.15	1.44
N,N-dimethylformamide	1.96	1.73
N-methyl-2-pyrrolidone	8.7	9.4
n-Hexane	0.1	0.61
Dichloromethane	0.21	1.16
Chloroform	1.3	4.6
Toluene	1.57	4.14
Chlorobenzene	1.62	3.4
o-Dichlorobenzene	1.91	8.94
1-Chloronaphthalene	1.8	8.1
Acetylacetone	1.5	1.02
Diethyl ether	0.72	0.4

2.4. Dispersion of reduced graphene oxide

Reduced graphene oxide (rGO) is produced by the reduction of GO, giving a material with properties closer to G [25]. The dispersibility of rGO is also closer to that of G (Table 1) [27]; although it disperses more effectively in polar solvents compared to G [10]. This is probably the result of residual carbon–oxygen containing functional groups; the carbon:oxygen ratio typically being around 12:1 [66,67].

The aqueous dispersibility of rGO is generally poor with aggregation occurring rapidly. However, there are reports of stable dispersions formed by the *in situ* reduction of aqueous GO solutions [68,69]. The *in situ* reduction negates the need for further sonication steps which appear to be less effective, are time consuming, and are likely to cause further damage to the rGO [70]. For comparison: the *in situ* reduction of GO in water concentration of 1.4 mg ml^{-1} [69] as opposed to 0.005 mg ml^{-1} by sonication of rGO powder [27].

The morphology of graphene and its derivatives can be affected by its processing, for example spray dried GO forms spherical, crumpled paper like aggregates by intra-sheet π–π stacking [71]. The result is a near spherical structure, a 44% reduction in surface area, and increased resistance to further aggregation [72]. Thermal reduction to rGO resulted

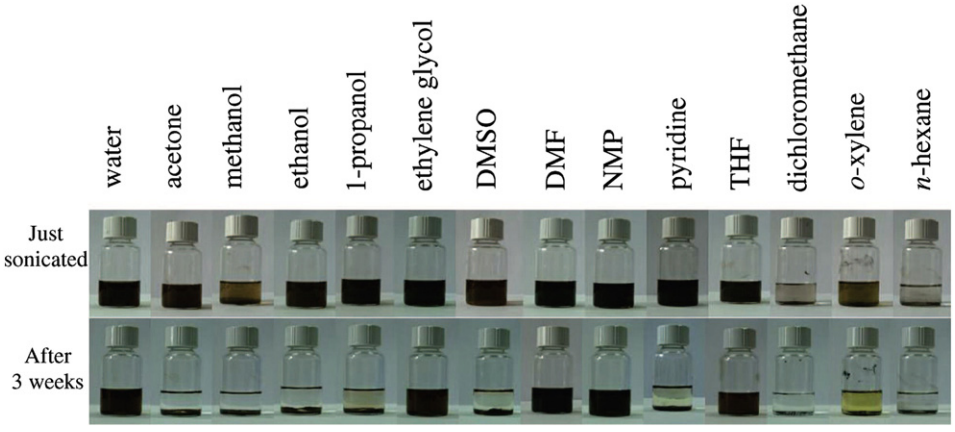

Fig. 3. The dispersion of GO in a range of solvents immediately after sonication (top) and after settling 3 weeks (bottom). Reprinted (adapted) with permission from Paredes et al. [51].

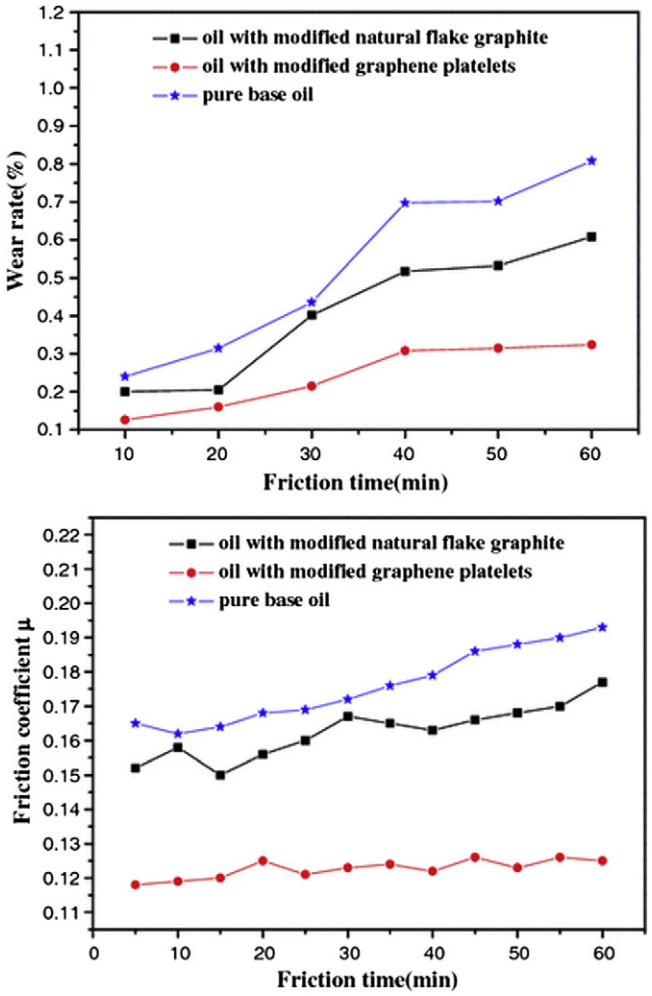

Fig. 4. Comparison of wear rate (top) and friction coefficient (bottom) as a function of friction time (four-ball, 1200 rpm, 147 N, 60 min, 75 ± 2 °C) for pure oil (blue), oil with graphene (red) and oil with graphite (black).
Reprinted (adapted) from Lin et al., with permission from Springer [83].

in a material with improved dispersibility in water, methanol, IPA, acetone, chloroform, THF toluene, cyclohexane dichlorobenzene and ethylene glycol with respect to flat rGO sheets [72].

3. Applications of graphene dispersions

The excitement surrounding graphene can be attributed to its wide range of potential applications [9,73,74]. While most applications do not employ graphene dispersions directly, many of them require graphene to be dispersed at some point during the process (e.g. the deposition of thin films of graphene). Therefore, the stability, concentration and overall quality of the dispersion remains extremely important.

3.1. Functional fluids

Graphene's high thermal conductivity, electrical conductivity, and inherent lubricity make it an ideal candidate for the modification of functional fluids. Adding a solid material with high thermal conductivity to a fluid to increase the overall thermal conductivity of the system is well known [75]. Having one of the highest thermal conductivities known in any material [3] makes graphene dispersions good candidates for use as thermal fluids. Yu et al. were the first to show the use of GO as an additive to improve the thermal conductivity of ethylene glycol [76]. GO nanosheets were prepared and dispersed in ethylene glycol at concentrations of up to 5 vol.% which gave thermal conductivity increases of up to 60% compared to pure ethylene glycol. Since this, other work has shown similar results in a range of other solvents, with the greatest improvement in thermal conductivity being observed in solvents with low thermal conductivities such as ethylene glycol [77]. However, the defects present in the structure of GO result in it having a lower thermal conductivity than pristine graphene or rGO [78,79]. For this reason attempts have also been made to increase the thermal conductivities of solvents using rGO [80–82]. However, rGO is inherently incompatible with many common solvents and so in most cases, either covalent modification or the use of surfactants is required. As an alternative to these methods, GO was first dispersed in both ethylene glycol and water and then reduced *in situ* using heating and NaOH to give a dispersion of rGO without the use of dispersants. Thermal conductivity measurements of these dispersions in ethylene glycol gave increases in thermal conductivity of up to 6.5% at 25 °C increasing to 36% at 50 °C (with a maximum thermal conductivity of 0.34 W m^{-1} K^{-1}), in spite of low concentrations of rGO (0.14 vol.%) being used. In water the increases seen were 14% and 94% at 25 and 50 °C respectively (with a maximum thermal conductivity of 1.26 W m^{-1} K^{-1} being measured) [69].

Dispersing graphene and its derivatives in functional fluids can also improve the tribological properties of the fluid. Lin et al. were one of the first to report the addition of graphene to a lubricant. In order to obtain good dispersions of graphene, dispersing agents including stearic acid and oleic acid were used, resulting in both the coefficient of friction and wear being greatly reduced (Fig. 4), more so than observed with the addition of graphite [83]. Other groups have since shown that the addition of graphene to lubricants can reduce wear and friction respectively by the following: 14% and 17% [84], 9% and 26% [85], and 33% and 80% [86] in base fluids ranging from water [87] to organic solvents [85] and oils [86,84].

3.2. Polymer composites

Dispersion of graphene in polymers is of significant interest as it promises to impart improved mechanical properties, electrical and thermal conductivity, and barrier properties to commodity polymers. To achieve many of these properties it is necessary to have percolation, an interconnected network of graphene, throughout the composite which is theoretically achieved at 0.1 vol.% [88]. However, in practice percolation can vary between from ~0.1–3 vol.% [89–92].

Dispersions of graphene in hydrophobic commodity and engineering polymers is challenging. The first problem is achieving a good dispersion in the polymer. This is partly addressed by either dispersing the graphene into a co-solvent with the polymer, before co-precipitation or drying to a film [70,89,93], or dispersing graphene in a monomer and polymerising *in situ* to produce a composite [94,95]. In an ideal situation solvent processed composites lock the graphene into its well dispersed form in the solvent; however, it is generally necessary to modify the graphene to improve its dispersibility and its interaction with the polymer matrix [96,97]. *In situ* polymerisation can give better results which may be due to the graphene participating in the polymerisation: grafting polymer chains on to graphene sheets [94].

Melt processing, direct dispersion into molten polymer typically gives poor results compared to solution based methods [98], and requires high volumes of filler [99]. This is likely to be partly due to the inherent low shears that can be achieved in high viscosity molten polymers. As a result reducing the polymer–graphene interfacial tension is expected to be even more important. This can be addressed by either the prior functionalisation of graphene [100], or by reactive blending in which the graphene reacts with the polymer under the process conditions [101]. In addition to functionalisation and dispersion

quality there are a number of other factors, such as graphene flake diameter and thickness that can impact on the performance of a polymer composite [102].

3.3. Thin films

Thin films of graphene have many potential applications including anti-bacterial sheets [103], electronic devices [104,105], organic photovoltaic devices [106], and transistors [107]. While it is common to produce these films directly from chemical vapour deposition, it is also possible to create them using techniques such as spray coating, drop casting or vacuum filtration [20,110,108,109]. However, when using these techniques it is important that the quality of the graphene dispersion is high. If this is not the case then the film's mechanical and electrical properties will be lacking [109].

Another consideration when creating thin films from dispersions of graphene is the solvent being used. While NMP can be used to produce stable, high concentration graphene dispersions it is also high boiling: making film deposition difficult. However, dispersion in volatile, low boiling point solvents is not trivial [27], and so in almost every case some form of modification must be used to stabilise the graphene dispersion [109]. An alternative approach to making films of graphene, arising from the good inherent solubility of GO in water, noted earlier, involves the production of thin films of GO and then, if required, reducing these either thermally or chemically in order to give a film with the properties of graphene [107,111,112].

3.4. Functional materials

Having a stable graphene dispersion allows controlled deposition to create free standing graphene films [113]. These are commonly produced either by filtration [114], casting [115], electrophoretic deposition [116], or layer by layer deposition [117]. In the case of layer by layer deposition graphene and a binder are alternately deposited from a dispersion. Common binders include nanoparticles [116,118,119], and polymers [117,120]. Composite materials may easily be produced by incorporating a filler or active material into the film either *via* the binder layer [121] or by co-deposition from the dispersion [122]. The resulting materials have found applications in sensors [123], super capacitors [121], and environmental remediation [124].

Both GO and rGO dispersions can be used to produce hydro- and organo-gels; a topic which has been recently reviewed [125]. As gelation occurs from graphene derivative dispersions it is possible to incorporate other materials, such as nanoparticles, into the gel to produce composite materials. Removal of the solvent phase produces 3D porous materials which find applications in energy storage [126], water purification [127,128], and gas adsorption [129].

Suitable gelation promoters for aqueous GO dispersions include among others: PVA [130], PEI, PEO, melamine, and multivalent metal cations [131]. In addition GO can spontaneously gelate in water by careful control of concentration and pH [131]. Gelation occurs either by hydrogen bonding or columbic attraction, the latter generally being stronger. In hydrogen bonded systems the sol to gel transition can be controlled by pH or ionic strength [130,131]. GO can also gelate in organic solvents, dependent of the lateral sheet size dimensions [132].

The reduction of aqueous dispersions of GO can result in the formation of rGO hydrogels, provided the GO concentration, temperature and reaction time are carefully controlled [133]. Similarly rGO organogels can be produced by the reduction of GO sheets in organic solvents [134].

3.5. Graphene inks

Inkjet printing of graphene is a technique that has emerged as a method of producing fine or complex patterns of graphene for use in applications such as sensors [135], printed electronics [136], antennas [137], and supercapacitors [138]. While the dispersions used for this technique require similar properties to those used in the production of thin films, there are some additional challenges that must be met. Inkjet printing typically requires inks with a particular viscosity and surface tension [139,140] which does not match well with the properties of the known good solvents for graphene [141]. Alongside this, high concentration dispersions are required to prevent the need for high numbers of print passes and to avoid aggregation, which may occur during drying [141].

In general, groups have attempted to overcome these challenges by using additives and stabilisers alongside graphene to alter the properties and stability of the dispersion. Common additives as viscosity modifiers and stabilisers include ethylene glycol [136], and ethyl cellulose [141,142].

As with thin films, an alternative to the production of graphene inks is to use the good dispersibility of GO in water to produce GO inks. This has the advantage that high loadings of GO can be used to increase the viscosity of the ink without the need for additives or stabilisers [137,138]. However, if these inks are used then an additional step of reduction must be performed after printing in order to restore the desired properties of graphene [138].

3.6. Environmental remediation

Graphene's extremely high surface area [12] has led to interest in the use of graphene or graphene derivatives for the removal of pollutants [143]. One of the key areas in this field is the removal of heavy metal ions from water sources [144]. As GO is soluble in water and has a relatively active surface, it is commonly the material of choice for those investigating this area; however, water dispersible forms of functionalised graphene are also of used [143]. Graphene derivatives have been shown to be able to successfully remove pollutants including the following: Cu(II) [145], Cd(II) [124,146], Co(II) [124], Zn(II) [146], Pb(II) [146–149], Hg(II) [150,151], Ni(II) [152], As(III) & (V) [153–155], and Cr(VI) [156] from water, as well as a range of organic dyes including methylene blue [157–159], and malachite green [158] among others [143]. For those interested in this field more in depth reviews are available [143,144].

3.7. Industrial perspectives on applications

In addition to the challenges already outlined, from a commercial or industrial perspective additional challenges exist; namely cost, stability, safety and end of life. The cost of producing a dispersible graphene and then dispersing it must be competitive. Stability during storage and transport must also be considered; the dispersion must be stable for a sufficiently long period of time to be useful. This stability must also extend to temperature, during transport and storage. Avoiding toxic and highly flammable solvents would be desirable and in some applications necessary. Additionally transporting large volumes of solvent is costly, so an ability to concentrate the dispersions for transport then dilution on site would be advantageous. Finally end of life and disposal must also be considered.

4. Functionalisation of graphene to aid dispersion

Given the limited range of solvents in which graphene disperses well, there is a lot of interest in its chemical functionalisation to produce modified graphenes with greater dispersibility in a wider range of solvents. In particular improving the dispersibility in water and volatile, low toxicity organic solvents is a priority for commercial application. Modification can be divided in to the non-covalent, involving the adsorption of molecules on to the graphene surface, or covalent involving chemical reaction with the graphene carbon atoms. Comprehensive reviews of graphene modification are presented elsewhere [160]; here

we summarise the most commonly encountered modifications used to improve graphene dispersion.

4.1. Non-covalent modification of graphene

The non-covalent modification of graphene and its derivatives has several advantages over covalent modification including the following: no dangerous chemistry, an abundance of commercially available modifiers, and the avoidance of damage to the graphene sp^2 network, which is essential to maintain many of its properties [160,161,162]. Therefore, non-covalent modification techniques lend themselves well to pristine graphene and GNP materials. Specific, non-covalent interactions have been reviewed elsewhere and include hydrogen bond–π, π–π, cation–π, and anion–π [160]. For the purposes of dispersions the principle interactions are π–π, cation–π, and hydrophobic effects; also emerging is the use of particles to maintain graphene dispersions.

From an industrial perspective non-covalent modification, especially with surfactants, is appealing because the process is relatively simple.

4.1.1. π–π interactions

The concept of π–π stacking is used to describe the non-covalent interactions involved in the stacking of aromatic molecules [163]. The extended, aromatic network of sp^2 carbon atoms makes this interaction important in graphene functionalisation. The precise nature of the π–π interaction is a matter of debate but in graphene appears to be a combination of dispersive and electrostatic interactions [164–167]. A variety of aromatic systems have been shown to interact with graphene including the following: polyaromatic hydrocarbons (PAH) [168–173], peptides [174,175], DNA [176], and conducting polymers [177–179]. As a means of functionalisation π–π is generally applied to pristine graphene, GNPs or rGO. This is because functional groups, as present in GO, disrupt the sp^2 network and the π–π interactions [180,181]. In the context of dispersions π–π stacking is used to tether groups which aid dispersion on the surface of sheets. This prevents graphene aggregation through sterics [168] or electrostatic repulsion [169].

By far the most common molecules used for π–π stacking are PAHs, and more particularly pyrenes. The binding strength as a function of PAH size is additive [165], and π–π bond strength has been shown to increase when the PAH is electron deficient [166].

Pyrene derivatives have been used to aid the dispersion of graphene either as small molecules [168–170], or as part of a polymer chain [171–173]. Green et al. conducted a detailed study comparing a series of pyrene derivatives for their ability to stabilise pristine graphene in aqueous solutions [169]. They found that charged pyrene derivatives performed best with the following trend sulfonyls > carboxylic acids > amines; salts were found to be particularly effective. This trend is presumed to be due to the electronegativity of the functional group, with the more electronegative sulfonyls increasing the strength of the π–π bond. The sodium salt of 1-pyrene sulfonic acid was found to give the optimal graphene dispersion at 0.33 mg ml^{-1} with improved thermal stability. Similarly Schlierf et al. compared a series of pyrene dyes containing varying numbers of sulfonyl and hydroxyl groups for the exfoliation of graphite [183]. Saturation of the graphite with dye occurred over several hours; dye absorption correlated to the molecule's dipole.

While the majority of the small molecule PAH literature focuses on electrostatics as a means of improving dispersion in water there are some examples where sterics are employed. For example adamantane functionalised pyrene is able to improve G dispersion in DMSO, DMF, THF and NMP *via* sterics [168].

Pyrene has also been used to tether polymer chains to graphene, either by the production of polymer chains end capped with pyrene [171,172,184,185], or by incorporating pyrene bearing monomer units into the polymer chain [186]. Pyrene chain ends are most frequently introduced *via* a pyrene based initiator [182,184,187] but can also be produced by modification of chain ends post-polymerisation (Fig. 5) [182].

A similar system using pyrene containing polymers was employed in the exfoliation of graphene in chloroform to 67.4 μg ml^{-1} [184]. Little work has been done on the influence of polymer chain molecular weight on dispersion and exfoliation, although molecular weights between 5 and 20 kDa seem to be efficient [185,182].

Copolymers in which one component binds to the graphene can also aid dispersion. Popescu et al. dispersed G in chloroform using copolymers of styrene and 2-vinylpyridine with both block and star architectures [188]. They achieved G concentrations of 0.29 and 0.22 mg ml^{-1} respectively. Protonation of the pyridine moieties decreased G concentration to 0.04 mg ml^{-1}; they attribute this to reverse micellisation of the copolymers. This indicates that the electron deficient pyridine ring binds more strongly to graphene than styrene. Oligohistidine bearing pyrene moieties have been used in the exfoliation and dispersion of graphene in water to 1 mg ml^{-1} [174,175]. Despite histidine being aromatic, and known to bind to graphene [189,190], it did not exfoliate graphene without the pyrene moiety being present. It may be that in water, the hydrophobicity of the pyrene plays a role in ensuring a strong interaction between the modifier and the graphene.

Conducting polymers, which are extended delocalised aromatic systems, have also been exploited for the non-covalent modification of graphene. Both polyaniline [177,178] and more particularly PEDOT [179] have been used to create dispersions. For example Jo et al. exploited PEDOT, doped with PSS to improve the aqueous solubility, to create water dispersible rGO at 0.4 mg ml^{-1} [179]. PEDOT, an electron rich thiophene aromatic, absorbs on to graphene to which a PSS layer subsequently absorbs; the dispersion is then maintained by electrostatic repulsion. PEDOT:PSS dispersions can be of sufficient quality to allow the production of conducting composite inks [191].

The stabilisation of graphene in water has also been achieved with DNA. Reduction of aqueous GO in the presence of single stranded DNA produced a stabilised rGO dispersions at 0.5–2.5 mg ml^{-1} for several months [176]. They also noted that using double stranded DNA was much less effective. Flavlin mononucleotides can also aid achieve aqueous dispersions of rGO up to 50 mg ml^{-1} [192]. It should be noted that DNA binding to graphene is often also discussed as resulting from hydrogen bonding or hydrophobic interactions [193,194].

4.1.2. Cation–π interactions

The cation–π interaction was introduced by Dougherty, who demonstrated that an electrostatic attraction can occur between a positive charge and the quadrupole moment of the aromatic ring [195]. The interaction is dominated by electrostatic and induction energies [196–198]. Cation–π interactions between rGO and monovalent inorganic cations involve a slow (several hours) but enthalpicaly favourable binding process which gives a qualitative increase in rGO dispersibility in water, DMSO and DMF [199]. Despite this, the metal cation–π interaction has not been widely exploited. Instead the focus has been on organic cations. The distinction between cation–π interaction and the π_{cation}–π has been discussed in detail elsewhere [160, 200]; briefly the π_{cation}–π is weaker than the cation–π interaction but stronger than the π–π interaction.

Imidazolium cations are often used [201], presumably because of their planar and aromatic structure. The nature of the counter ion is known to be important. Ghatee and Moosavi examined theoretically the absorption of various organic cations (ionic liquids) on graphene [202]. They found the steric bulk of the cation has only a marginal effect on the adsorption of ionic liquids on graphene but the anion identity has a large effect; PF_6^- giving a stronger adsorption than $C1^-$. The calculated ΔH_{ads} being -90 kJ mol^{-1} for Cl^- and -10 kJ mol^{-1} for PF_6^- respectively.

Gao et al. demonstrate an aqueous dispersion of rGO with an imidazolium modified polyether [203]. The aqueous *in situ* reduction of GO in the presence of hydroxyl bearing ionic liquids allowed for

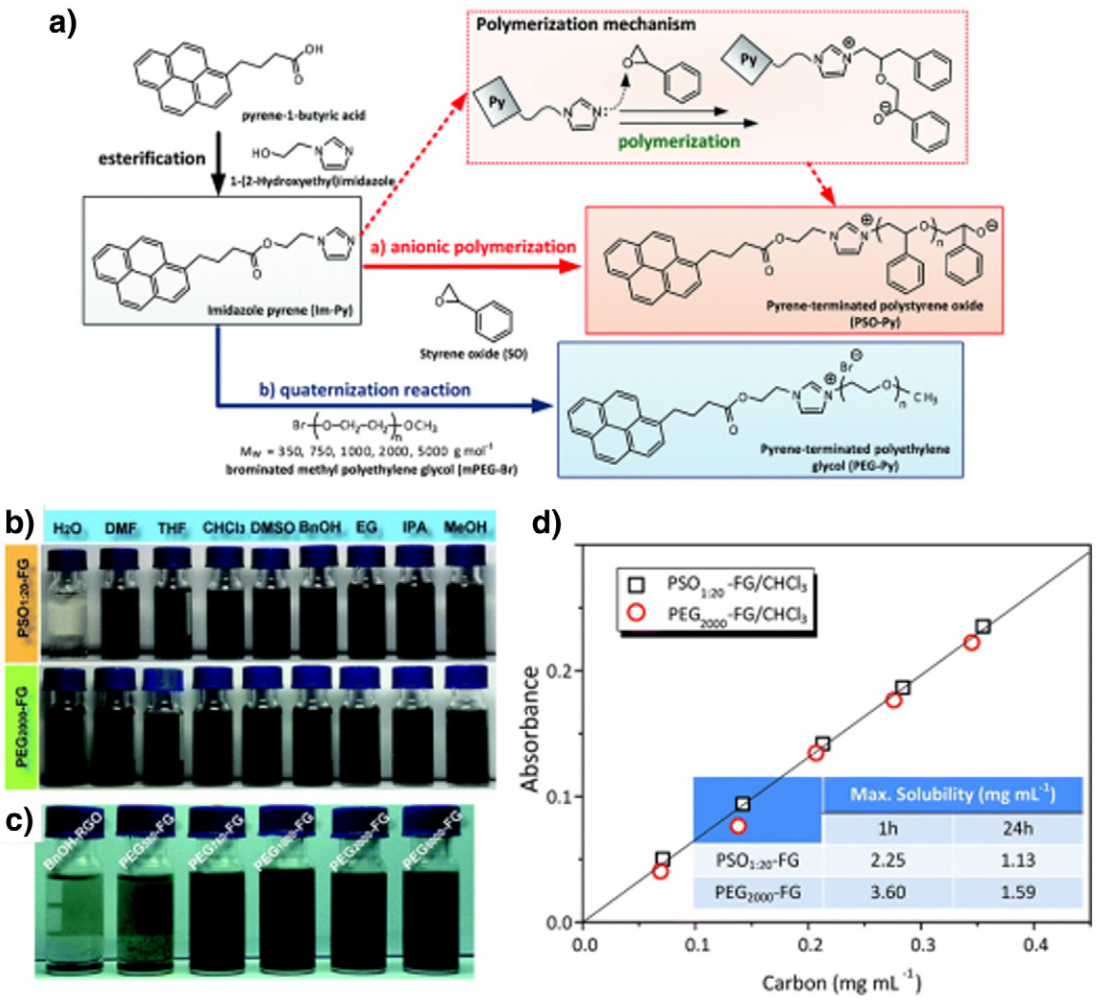

Fig. 5. (a) Graft from and graft to approaches toward pyrene containing polymers of polystyrene oxide (PSO-Py) and polyethylene glycol (PEG-Py). (b) Digital photo of PSO functionalised graphene (PSO1:20-FG) and PEG functionalised graphene (PEG-FG) with different chain lengths dispersed in various organic solvents by bath sonication (<5 min). (c) Photograph of PEG-FG with different chain lengths dispersed in chloroform by bath sonication (<5 min). (d) Optical density at 500 nm of polymer functionalised graphene in chloroform at different concentrations.
Reproduced from [182] with permission of Royal Society of Chemistry.

successful dispersion in ethanol, chloroform, THF, toluene and, to a lesser extent, water. The hydroxyl groups were successfully used to initiate the polymerisation of ε-caprolactone [204].

4.1.3. Surfactants

Of all the classes of non-covalent modifiers for the dispersion of graphene surfactants are perhaps the most promising as there are a wide variety available commercially.

Hsieh et al. examined the adsorption of SDS onto rGO surfaces by conductometric titration, and identified several stages that occur at increasing SDS concentrations: adsorption at the basal plane edges, complete coverage of the rGO, and finally the formation of surface micelles [205]. The same group also examined the effect of SDS concentration on rGO dispersibility in water. At [SDS] < 10 μM rGO quickly re-aggregated. Aggregation was suppressed as the [SDS] increased and at [SDS] > 40 μM the dispersions were stable for over a year [206]. Fernández-Merino et al. compared the stabilisation of aqueous rGO by a variety of surfactants at different pHs (Fig. 6) [110].

Surfactants with planar hydrophobic tails, and a capacity for π–π bonding, performed best at dispersing G: in particular SDBS. The importance of surfactant microstructure is emphasised in the relative performance of sodium cholate to sodium deoxycholate when dispersing graphene in water, giving estimated concentrations of 0.52 and 2.58 mg ml^{-1} respectively; this is attributed to the absence of oxygen at aromatic centre of sodium deoxycholate improving its ability to bind with graphene [207]. Studies on peptide binding also suggest planar and small side groups aid strong adsorption which leads to good dispersion [190].

For non-ionic surfactants in aqueous dispersions the conceptual model is that the hydrophobic domains absorb to the graphene, and the hydrophilic domains maintain the dispersion. This appears to be the case for Pluronic (PEO-b-PPO-b-PEO) copolymer with rGO [110] and GO [208,209]. In the case of Pluronic copolymers the length of the hydrophilic PEO block appears to correlate with the aqueous dispersion's stability [208,209].

However, not all non-ionic surfactants are block copolymers; one of the most widely used non-ionic surfactants is PVP where each monomer repeat unit is effectively a surfactant [210–212]. PVP has been widely used to aid the exfoliation of graphene [213] and for the dispersion of rGO [214] in aqueous conditions to concentrations as high as 6.22 mg ml^{-1} [210]. PVP is also known to aid the exfoliation of graphene in organic solvents including the following: NMP, DMSO, DMF, IPA, ethanol and methanol and water [215].

Various other polymeric surfactants have also been shown to stabilise graphene dispersions in water and organic solvents including the following: PEI [216], PSS [88,217] and PVAc latex [218] at

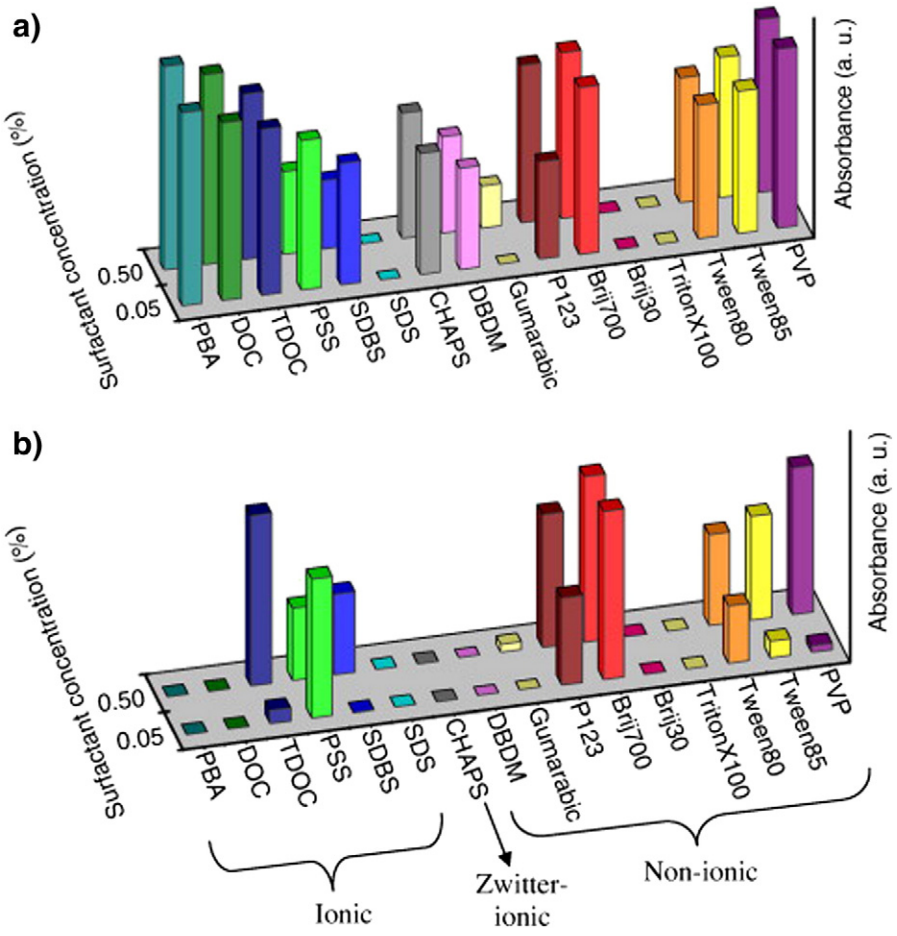

Fig. 6. UV–vis absorbance at 450 nm measured on the supernatant of centrifuged (10,000 *g*, 10 min) surfactant stabilised 0.1 mg ml^{-1} dispersions at pH 12 (a) and pH 1 (b). Two surfactant concentrations are shown, 0.05% and 0.50% wt/vol.
Reprinted (adapted) from Fernández-Merino et al., with permission from Elsevier [110].

concentrations of up to 2 mg ml^{-1}, 0.110 mg ml^{-1}, and 20 mg ml^{-1} in water respectively. Bespoke polymers have been used to aid the exfoliation of graphite producing stable graphene dispersions at high concentration of up to 50 mg ml^{-1} [219].

4.1.4. Particles

Non-covalent modification *via* nanoparticles added to the surface of graphene has been proposed as a way of improving dispersibility. Particles act in a slightly different way to other non-covalent modifiers because their size, when adsorbed onto the surface of graphene, means they act as a barrier to the reaggregation of sheets: as well as potentially improving compatibility with the solvent (Fig. 7) [220]. This process generally involves the *in situ* synthesis of nanoparticles in the presence of graphene. For example silica nanoparticles grown and calcined *in situ* from silanes on GO have improved dispersibility in water and ethanol even after the GO is thermally reduced [220]. Similarly, magnesium phyllosilicate clay functionalised with an amino silane can be used to improve the dispersion of rGO in water: giving concentrations of up to 7.5 mg ml^{-1} [221]. Surfactant coated polyoxometalate clusters (POMs) can be used to transfer rGO from water to chloroform: a result which could not be achieved with surfactant alone [222].

Organic and inorganic nanoparticles have been used to exfoliate graphite producing high concentration dispersions of graphene [223–225]. For example carbon dots have been shown to exfoliate graphite and disperse the resulting graphene to concentrations of up to 0.4 mg ml^{-1} in water [225].

4.2. Covalent modification of graphene

Graphene's inherent inertness makes its covalent modification a difficult process. In spite of this, methods for the production of many different forms of covalent modification graphene and its derivatives are presented in the literature. Functionalisation can be performed with many different end goals in mind [74,160,226]. However, this section will focus on those covalent functionalisation techniques most relevant to improving the dispersibility of graphene and related materials.

4.2.1. Covalent functionalisation of pristine graphene

While research into the covalent modification of G has produced a range of functionalisation techniques [160,227,228], it is not an area that has attracted much attention for the production of dispersions. The reason for this is that for applications that require dispersible G, non-covalent modifiers are usually the better option as they often have to be used during the exfoliation of G.

4.2.2. Functionalisation of GO based materials

An alternative route to functionalised graphene is to use GO as a starting material. While GO is already a form of covalently functionalised graphene, it is often categorised as a material in its own right [18]. Many groups have taken advantage of GO's increased chemical reactivity and used it as a starting material in the production of functionalised graphene.

Functionalisation can be performed on either GO [229] or on rGO [230,231] as some defect sites remain even after reduction. Each of

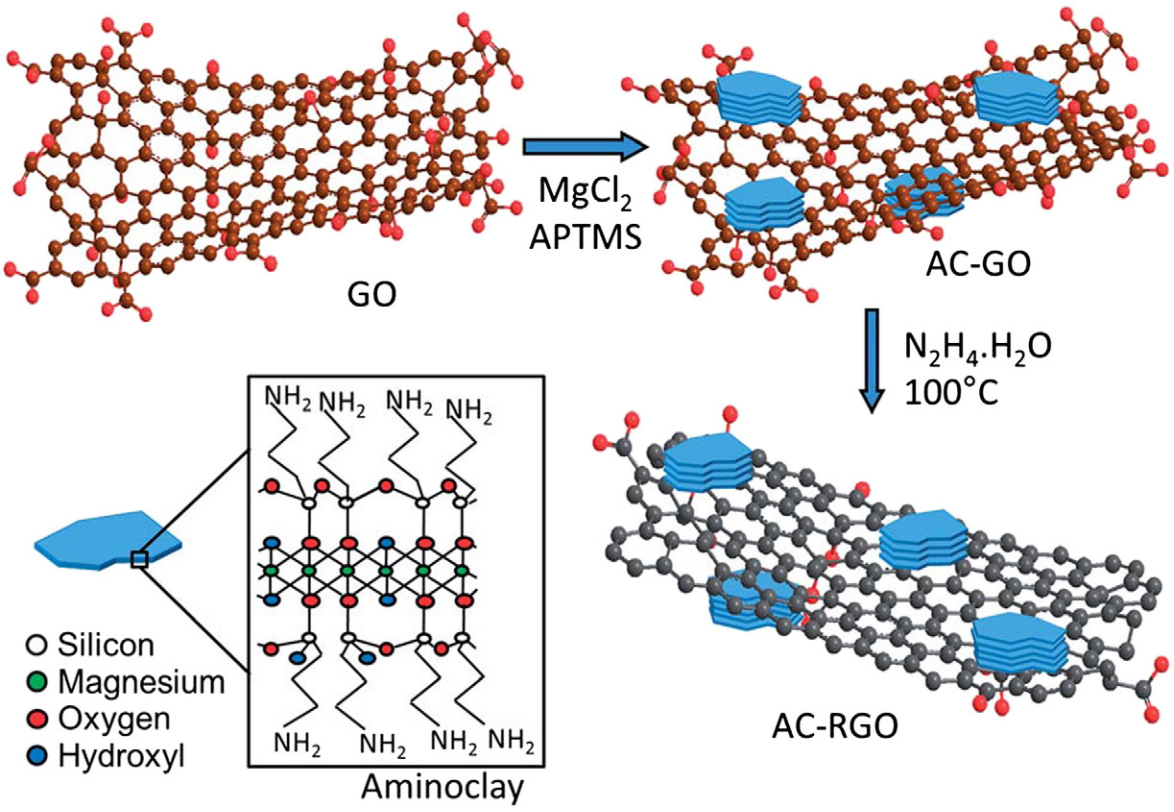

Fig. 7. *In situ* preparation of aminoclay-GO and aminoclay-rGO hybrids. The blue platlets depict aminoclay, the brown and grey sheet depict GO and rGO respectively. Reproduced from [221] with permission of Royal Society of Chemistry.

these routes has its own advantages and disadvantages. If functionalisation is performed on GO then the reduction step may be hindered as the new functional groups on the surface could prevent the removal of oxygen functionalities, or may even be removed in the reduction [232]. If reduction is performed prior to functionalisation then the number of potential reaction sites is greatly reduced and so the degree of functionalisation is likely to be less [48].

4.2.3. Starting from GO

While GO is an ideal candidate to use for covalent functionalisation due to its already high level of functionality, the exact identity and distribution of the oxygen containing groups on its surface is still under debate [48]. It is widely believed that there are a range of epoxide, ether, aldehyde, ketone, alcohol, and carboxylic acid groups present on the sheets [45–48]. This means that a variety of different reactions and chemistries can be used to covalently functionalise GO.

The presence of carboxylic acid groups on GO allows small molecules to be coupled to the GO *via* amide or ester bonds. In order to functionalise at these sites, GO carboxylic acids must be activated in order to increase their reactivity [48]. The reagents used to do this include some commonly used for peptide synthesis such as EDC [233–235], DCC [236,237], and HATU [238,239], and others more commonly found in synthetic organic chemistry such as thionyl chloride ($SOCl_2$) [240–243]. Once this activation has occurred the GO carboxylic acids readily react with molecules containing functionalities such as amines, to form amide bonds [234,235], and hydroxyls, to form esters [160,236,237]. By selecting molecules that have similar chemistries to the desired solvents, the dispersibility of graphene in a variety of solvents can be greatly improved. Octadecylamine, dodecylamine, and hexadecylamine functionalised rGOs showed improved dispersibility of over 3 mg ml^{-1} in solvents with Hansen parameters of $6.3 < (\delta_p + \delta_h) < 13.7$ such as toluene, chloroform, and chlorobenzene [229].

An alternative approach to functionalisation presented by Stankovich et al. involved the conversion of carboxylic acid and alcohol groups present on GO into different reactive functional groups, including amides and carbamate esters through the use of a range of isocyanate functionalised hydrocarbons [88]. This process resulted in an increase in the dispersibility of GO in DMF, NMP and DMSO.

Carboxylic acid groups only make up part of the oxygen content of GO, and are generally believed to be located at the edges of sheets. Therefore an alternative approach is to target the other functional groups present, most commonly the epoxide group. Functionalisation by the ring opening of epoxides can proceed *via* a number of methods including the use of sulphur nucleophiles such as potassium thioacetate [244], the conversion of epoxy groups to hydroxyl groups by the use of by TRIS [245], and the use of malononitrile which adds to the epoxide group to leave pendent nitrile groups which can then be further functionalised [246].

Another approach to the covalent functionalisation of graphene oxide is the use of silanes as a modifier. Functionalisation occurs by a reaction between hydroxyl groups on the GO surface and the trialkoxy groups present on the silanes, after which reduction can be performed to form functionalised rGO [247]. Silanes can be used to improve the dispersibility of GO in a wide range of media. Reaction of GO with EDTA–silane formed EDTA–rGO which could be dispersed in water [247]. An alternative approach involved the functionalisation of GO with GPTMS to form silane functionalised GO which then showed improved dispersibility in epoxy resin for use in nanocomposites [248].

As well as the covalent functionalisation of GO with small molecules, it is also possible to functionalise GO with polymer chains, or to even initiate polymer growth off the surface of a GO sheet. ATRP can be used to functionalise GO with poly(tert-butyl acrylate) which can be

readily dispersed in toluene at 1 mg ml^{-1} [249]. Also using ATRP, Lee et al. improved the solubility of GO in a variety of both polar and non-polar organic solvents including DMF, toluene, chloroform, and methylene chloride, up to 30 mg ml^{-1}, *via* the formation of surface initiated poly(styrene) on GO [250].

4.2.4. Starting from rGO

Functionalisation of rGO, which has had the majority of its oxygen functionalities removed, tends to involve more similar reactions to those performed on pristine graphene than those performed on GO. However, it is possible to add functionality at the residual oxygen containing groups on the material [251,252]. One of the most popular routes for the functionalisation of rGO is the use of diazonium salts. These can be used to add a range of functional groups to rGO [230,231,253–255]. While rGO has greater potential for functionalisation than G, due to being open to both graphene-like and GO-like covalent functionalisations, it is little used. However, Shen et al. were able to produce amphiphilic rGO functionalised by polystyrene–polyacrylamide copolymers, improving the dispersibility of rGO in both water and xylene, and claim this to be a universal way of improving compatibility of rGO as the hydrophilic–hydrophobic balance of the copolymer can be controlled to improve interactions with a wide range of polymers or solvents [251].

4.3. Challenges associated with the characterisation of functionalised graphene

As has been previously discussed in this section, both covalent and non-covalent methods for the functionalisation of graphene and GO have their advantages and disadvantages. However, within the literature there remains considerable ambiguity over which routes functionalisation is occurring by. In many cases it may be that the functionalisation occurring is, in reality, based on a mix of interactions. From a scientific perspective this is something which merits further investigation. However, from an industrial perspective this is of less importance as the results achieved remain the same. Routes created to produce covalently functionalised graphene, by design, involve reagents which will interact together favourably and so a considerable degree of non-covalent functionalisation may also occur, be it ionic, π–π stacking, cation–π, or dipole based. Due to the strength of some of these interactions functionalising reagents that are not covalently attached can still be extremely difficult to remove from the surface of the graphene.

4.4. Restoring the properties of graphene

The modification of graphene and graphene derivatives to improve its dispersibility does have a negative impact on the physical properties of the material, generally due to the disruption of the extended sp^2 hybridisation found in graphene (Table 2) [110]. Therefore, there is often a desire, as a final step, to remove any modifiers: restoring the properties of the graphene.

Table 2
Percentage rGO vs conductivity and specific capiciatance in paper like films cast from surfactant rGO dispersions.
Reprinted (adapted) from Fernández-Merino et al., with permission from Elsevier [110].

Film	rGO/wt.%	Conductivity/S m^{-1}	Specific capacitance/F g^{-1}
RGO	100 (~12 mg)	7548	38
RGO/PBA	36	13.31	1
RGO/DOC	47	0.06	1
RGO/TDOC	36	2.18	3
RGO/PSS	41	10.51	114
RGO/SDBS	29	0.87	7
RGO/SDS	87	4679	46
RGO/CHAPS	36	0.92	2
RGO/DBDM	11	0.01	3
RGO/P-123	38	5.53	12
RGO/Brij700	10	1.08	6
RGO/Tween 80	13	0.41	95

In applications where the end product is not a dispersion the removal of modifiers usually involves washing or thermal annealing. However, the nature of the end application may limit what can actually be achieved, for example GO printed on paper could not be thermally annealed to high reduction temperatures (>500 °C) without damaging the paper; as a result only partial de-functionalisation may be possible [25]. By contrast washing may be more mild but is only an option in non-covalently modified G and requires substrates to be compatible with washing solvents.

In order to reduce the impact of this problem, the amount of modifier can be minimised while still in dispersion using a strategy outlined by Irin et al. [256]. They compared different techniques for removing unabsorbed surfactants and found that vacuum filtration > dialysis > spray drying for PVP and PSA. However, in terms of maintaining colloidal stability: dialysis > vacuum filtration > spray drying; which is unsurprising given that the latter two require the material to be removed from dispersion then re-dispersed.

5. Characterisation

The stability of a dispersion can only be defined based on the application it is destined to be used for and what the important properties are in this application. Some dispersions, which may need to be stored for a long time can only be considered to be stable if there is no change in concentration over this time period. In other systems sedimentation is unimportant, for example fruit juice can exhibit pulp settling without the quality of the product being affected [257].

Graphene characterisation is a complex area encompassing electrical, spectroscopic, and microscopic methods and has been reviewed elsewhere [258,259]. However, in relation to dispersions the property that principally needs to be determined is the concentration, relative or absolute, of graphene and the variation of this over time.

5.1. UV–vis

A commonly applied method of determining concentration is UV–vis spectroscopy. The UV absorption in graphene is dominated by the $\pi \rightarrow \pi^*$ C = C plasmon transition at $\lambda_{max} < 300$ nm [260]. The absorbance at >500 nm is flat, but the optical density is dependent on concentration. As a result this area of the spectrum is often used to determine concentration according to the Beer–Lambert law. This requires the use of an absorption coefficient: usually designated α. The absorption coefficient for graphene has been shown to vary widely between samples, for example Coleman's group reports α in independent experiments ranging between 1390 and 6600 ml mg^{-1} [16,20,261,262]. Su et al. investigated the important parameters in determining absorption coefficients for rGO dispersions in NMP, from which they conclude that in rGO and G α is proportional to three variables: lateral sheet size, number of layers, and number of functional groups [263]. Consequently, care must be taken when using literature values of α, as should applying a single value of α across a series of differently processed or functionalised samples. However, in spite of this, UV–vis remains the most convenient method of determining the dispersion concentration and stability.

An alternative method of measuring concentration is simply to isolate and weigh the dispersed graphene, either by conventional drying to constant mass or by thermogravimetric analysis [264]. While simple this method requires large amounts of material which can be inconvenient especially when performing sedimentation and stability studies

There is no consensus in the literature as how to best prepare the samples. For example it is common to both immediately measure the as prepared dispersion, and to allow larger particles to sediment out. The latter is often achieved either by “mild” centrifugation [206,260] or by allowing the solution to stand over an certain length of time [51, 265].

5.2. Light scattering

Light scattering is a technique which can be used to determine both the size and shape of colloidal particles. Light scattering is divided in to two forms: static (SLS) and dynamic (DLS). The former ignores the motions of the particles, while the latter uses the motion to determine particle size [266]. Unless more specialist models are applied: most commercial equipment will tend to model for spherical scattering. Consequently, sizes obtained are sphere equivalent sizes rather than absolute values [266]. The validity of both techniques is undermined by multiple scattering, occurring off more than one particle, which is particularly problematic for large particles, concentrated colloids, or for particles which have high refractive index contrast with the medium. However, with these limitations in mind it is still possible to gain useful data from light scattering.

SLS can provide data on both particle size and shape by measuring scatter intensity at multiple angles simultaneously. However, for particles with size ≥ the laser wavelength, the models for non-spherical particles are incomplete [266]. In graphene–THF colloids, the graphene was confirmed to be a large flat disk, but size could only be determined to be >1 μm [267]. While it is possible to find numerical solutions for particles of arbitrary size and shape, these have limited validity in polydisperse systems. Consequently for the casual user SLS is most likely to be useful for determining sphere equivalent sizes.

In DLS particle size is determined via the diffusion coefficient; an autocorrelation function is used to monitor the temporal change in scatter intensity as the particles move under Brownian motion. This can then be used to calculate a particle size, typically as a sphere equivalent [266]. In non-spherical particles like graphene a more physically real description of size has to account for two diffusion coefficients: lateral and rotational. Such models have been successfully used to fit graphene DLS data, though they are difficult to work with [267]. A less cumbersome approach was proposed by Lotya et al. who developed an empirical model to convert sphere equivalent sizes to graphene flake sizes although this fails to account for particle polydispersity [268].

The difficulties in using light scattering mean that, for the casual user, sphere equivalent sizes combined with microscopy techniques on dried down colloids remain the most accessible route to particle sizing.

5.3. Zeta potential

When a material is immersed in a solvent a charge may develop at the interface creating a potential; graphene in water is typically negatively charged [269,270]. This may be modelled as an electric double layer, in which there are three distinct regions: a closely bound layer of oppositely charged ions (Stern layer), a diffuse layer and then the bulk solvent (Fig. 8). Located somewhere within the diffuse layer is the shear (slip) plane, below which all the components move as a single kinetic unit with the particle. The potential at this shear plane is defined as the zeta (ζ)-potential. This potential often correlates strongly to dispersion stability with higher magnitude zeta potentials ($|\zeta|$) being more stable due to electrostatic repulsion between particles. This is affected by temperature, solvent, ionic strength and pH [271]. The detailed discussion of colloidal stability over different timescales is discussed elsewhere in detail [271]. However, as a general guide $|\zeta|$ of 0–10 mV will be unstable, 10–30 mV will be slightly to moderately stable, 30–60 mV will have good stability, and >60 mV will have excellent stability for electrostatically repelling particles [272]. Although it should be noted that sterically stabilised colloids can be stable without large ζ-potentials [273].

Direct measurement of ζ is not possible, rather the particle's electrophoteric mobility is measured. In modern commercial equipment this is routinely measured by electrophoteric light scattering: the process being simple and very fast [273]. The particle's velocity is measured in an electric field by monitoring the Doppler shift in scattered light [273]. The electrophoteric mobility can then be applied to a model to obtain ζ. There are several specialist models, but two classical models Hückel and Smoluchowksi are the most commonly applied as each represents an extreme. Doane et al. discuss model choice in detail, but for large (μm), colloidal particles with large radius of curvature, the Smoluchowski model is generally the more appropriate [273]. This is convenient as the Smoluchowski model does not depend on particle shape. However, exceptions may exist at low ionic strength or in organic solvents [271].

For both GO and rGO in water between pH 3 and 12 ζ is negative [270], reflecting the pK_a of the oxygen functionalities present [274]. However, GO is stable from pH 4–11.5 whereas rGO is stable only between pH 8–11.5. This corresponds with $|\zeta| > 30$ mV which is achieved at approximately pH 4 and 8 for GO and rGO respectively. This has been attributed to the deprotonation of different groups; GO being stabilised at relatively low pH due to negatively charged carboxylates; whereas, rGO stability relies on the deprotonation of phenolic group which only occurs at higher pH [270].

Liu et al. mapped the ζ-potential of G exfoliated in several organic solvents including the following: benzoyl chloride, 1,2-dichlorobenzene, GBL, DMF, and NMP among others [269]. In all solvents the dispersed G was found to have $|\zeta| \geq 30$ mV. Foll all solvents studied, other than benzyl chloride and dicholorbenzene, ζ was negative. This is attributed to Lewis charge transfer of interfacial solvent molecules and the graphene.

5.4. Long term stability of dispersions

The long term stability of a dispersion is a quality that is extremely important for many commercial applications of graphene. It is however,

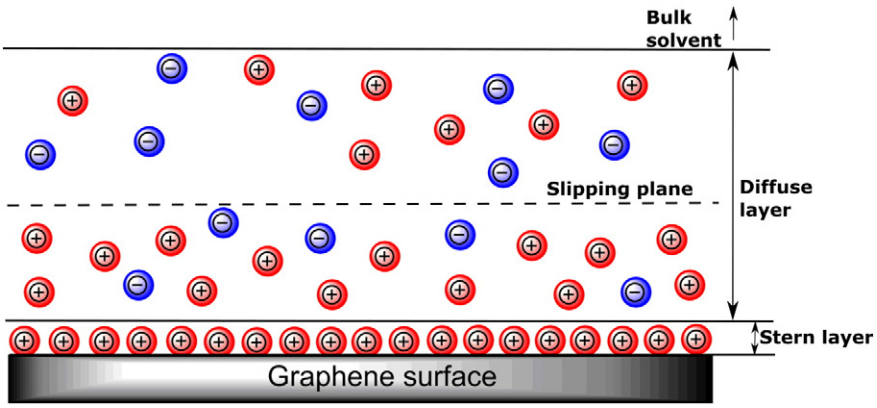

Fig. 8. A schematic of the ζ-potential double layer model for a negatively charged graphene sheet.

unfortunately one that is often ignored in many scientific publications. The only definitive method to determine the long term stability of a graphene dispersion is to observe its concentration over a long time period, looking for any change in its quality (either directly measuring concentration or another important property such as conductivity, viscosity etc.). Unfortunately this process is often a bottleneck in research and development of dispersions and so several techniques are available to accelerate it. These include centrifugation, mixing and agitation, thermal procedures, and physico-chemical methods [257]. It should however, be noted that these techniques may induce additional destabilisation which would not be observed under normal conditions [257].

6. Conclusion

The importance of stable dispersions for the commercialisation of graphene cannot be overstated. In this review several applications are highlighted in which end users will require graphene dispersion which are tolerant to batch to batch variabilities between formulations, have long shelf lives or else are trivially re-dispersed.

Currently the literature overly relies on sonication, which will be limiting in large volume applications. Consequently alternatives to sonication such as high shear mixing or ideally simple agitation are a priority. In addition there is a need to increase the concentration of graphene dispersions, the cost and risk of transporting and storing large dilute solutions is potentially high; end users may also wish to dilute concentrate dispersions into their own formulations. Therefore, there is a need to address the long term evolution and stability of graphene dispersions. While characterisation of dispersions can be both difficult and time-consuming, it should not be prohibitive provided the limitations of current techniques are understood.

Despite these challenges we have highlighted the considerable successes of the field, in particular the increase in dispersed graphene concentration from $\mu g\ ml^{-1}$ to $mg\ ml^{-1}$, over the last ten years. Moreover the range of solvents has also increased to include more volatile and less toxic alternatives to NMP, DMF etc. While the cost effectiveness of the modifications and processes used is still unclear, they demonstrate the principle that the challenges of working with graphene can be overcome.

Acknowledgements

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References

[1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. Science 2004;306:666–9.
[2] Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P, Stormer HL. Ultrahigh electron mobility in suspended graphene. Solid State Commun 2008;146:351–5.
[3] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, Lau CN. Superior thermal conductivity of single-layer graphene. Nano Lett 2008;8:902–7.
[4] Bunch JS, Verbridge SS, Alden JS, van der Zande AM, Parpia JM, Craighead HG, McEuen PL. Impermeable atomic membranes from graphene sheets. Nano Lett 2008;8:2458–62.
[5] Du X, Skachko I, Barker A, Andrei EY. Approaching ballistic transport in suspended graphene. Nat Nanotechnol 2008;3:491–5.
[6] Castro Neto AH, Guinea F, Peres NMR, Novoselov KS, Geim AK. The electronic properties of graphene. Rev Mod Phys 2009;81:109–62.
[7] Nair RR, Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, Peres NMR, Geim AK. Fine structure constant defines visual transparency of graphene. Science 2008;320:1308.
[8] Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 2008;321:385–8.
[9] Edwards RS, Coleman KS. Graphene synthesis: relationship to applications. Nanoscale 2013;5:38–51.
[10] Ayán-Varela M, Paredes J, Villar-Rodil S, Rozada R, Martínez-Alonso A, Tascón J. A quantitative analysis of the dispersion behavior of reduced graphene oxide in solvents. Carbon 2014;75:390–400.
[11] Everett DH. Basic principles of colloid science. London: The Royal Society of Chemistry; 1988.
[12] Qin Z, Taylor M, Hwang M, Bertoldi K, Buehler MJ. Effect of wrinkles on the surface area of graphene: toward the design of nanoelectronics. Nano Lett 2014;14:6520–5.
[13] Coleman JN. Liquid exfoliation of defect-free graphene. Acc Chem Res 2013;46:14–22.
[14] Hong BJ, Compton OC, An Z, Eryazici I, Nguyen ST. Successful stabilization of graphene oxide in electrolyte solutions: enhancement of biofunctionalization and cellular uptake. ACS Nano 2012;6:63–73.
[15] Hernandez Y, Lotya M, Rickard D, Bergin SD, Coleman JN. Measurement of multicomponent solubility parameters for graphene facilitates solvent discovery. Langmuir 2010;26:3208–13.
[16] Khan U, Porwal H, O'Neill A, Nawaz K, May P, Coleman JN. Solvent-exfoliated graphene at extremely high concentration. Langmuir 2011;27:9077–82.
[17] Kuila T, Bose S, Mishra AK, Khanra P, Kim NH, Lee JH. Chemical functionalization of graphene and its applications. Prog Mater Sci 2012;57:1061–105.
[18] Bianco A, Cheng HM, Enoki T, Gogotsi Y, Hurt RH, Koratkar N, Kyotani T, Monthioux M, Park CR, Tascon JM, Zhang J. All in the graphene family a recommended nomenclature for two-dimensional carbon materials. Carbon 2013;65:1–6.
[19] Hernandez Y, Nicolosi V, Lotya M, Blighe FM, Sun Z, De S, McGovern IT, Holland B, Byrne M, Gun'ko YK, Boland JJ, Niraj P, Duesberg G, Krishnamurthy S, Goodhue R, Hutchison J, Scardaci V, Ferrari AC, Coleman JN. High-yield production of graphene by liquid-phase exfoliation of graphite. Nat Nanotechnol 2008;3:563–8.
[20] Lotya M, Hernandez Y, King PJ, Smith RJ, Nicolosi V, Karlsson LS, Blighe FM, De S, Wang Z, McGovern IT, Duesberg GS, Coleman JN. Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions. J Am Chem Soc 2009;131:3611–20.
[21] Herron CR, Coleman KS, Edwards RS, Mendis BG. Simple and scalable route for the 'bottom-up' synthesis of few-layer graphene platelets and thin films. J Mater Chem 2011;21:3378–83.
[22] Green AA, Hersam MC. Solution phase production of graphene with controlled thickness via density differentiation. Nano Lett 2009;9:4031–6.
[23] Stankovich S, Piner RD, Chen X, Wu N, Nguyen ST, Ruoff RS. Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). J Mater Chem 2006;16:155–8.
[24] Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, Ruoff RS. Graphene and graphene oxide: synthesis, properties, and applications. Adv Mater 2010;22:3906–24.
[25] Pei S, Cheng HM. The reduction of graphene oxide. Carbon 2012;50:3210–28.
[26] Shang Y, Zhang D, Liu Y, Guo C. Preliminary comparison of different reduction methods of graphene oxide. Bull Mater Sci 2015;38:7–12.
[27] Konios D, Stylianakis MM, Stratakis E, Kymakis E. Dispersion behaviour of graphene oxide and reduced graphene oxide. J Colloid Interface Sci 2014;430:108–12.
[28] Alaferdov A, Gholamipour-Shirazi A, Canesqui M, Danilov Y, Moshkalev S. Size-controlled synthesis of graphite nanoflakes and multi-layer graphene by liquid phase exfoliation of natural graphite. Carbon 2014;69:525–35.
[29] Kim K, Park HJ, Woo BC, Kim KJ, Kim GT, Yun WS. Electric property evolution of structurally defected multilayer graphene. Nano Lett 2008;8:3092–6.
[30] Hao F, Fang D, Xu Z. Mechanical and thermal transport properties of graphene with defects. Appl Phys Lett 2011;99:041901.
[31] Ravula S, Baker SN, Kamath G, Baker GA. Ionic liquid-assisted exfoliation and dispersion: stripping graphene and its two-dimensional layered inorganic counterparts of their inhibitions. Nanoscale 2015;7:4338–53.
[32] Texter J. Graphene dispersions. Curr Opin Colloid Interface Sci 2014;19:163–74.
[33] Shih CJ, Lin S, Strano MS, Blankschtein D. Understanding the stabilization of liquid-phase-exfoliated graphene in polar solvents: molecular dynamics simulations and kinetic theory of colloid aggregation. J Am Chem Soc 2010;132:14638–48.
[34] Arao Y, Kubouchi M. High-rate production of few-layer graphene by high-power probe sonication. Carbon 2015;95:802–8.
[35] O'Neill A, Khan U, Nirmalraj PN, Boland J, Coleman JN. Graphene dispersion and exfoliation in low boiling point solvents. J Phys Chem C 2011;115:5422–8.
[36] Polyakova (Stolyarova) EY, Rim KT, Eom D, Douglass K, Opila RL, Heinz TF, Teplyakov AV, Flynn GW. Scanning tunneling microscopy and X-ray photoelectron spectroscopy studies of graphene films prepared by sonication-assisted dispersion. ACS Nano 2011;5:6102–8.
[37] Skaltsas T, Ke X, Bittencourt C, Tagmatarchis N. Ultrasonication induces oxygenated species and defects onto exfoliated graphene. J Phys Chem C 2013;117:23272–8.
[38] Liu L, Shen Z, Yi M, Zhang X, Ma S. A green, rapid and size-controlled production of high-quality graphene sheets by hydrodynamic forces. RSC Adv 2014;4:36464–70.
[39] Paton KR, Varrla E, Backes C, Smith RJ, Khan U, O'Neill A, Boland C, Lotya M, Istrate OM, King P, Higgins T, Barwich S, May P, Puczkarski P, Ahmed I, Moebius M, Pettersson H, Long E, Coelho J, O'Brien SE, McGuire EK, Sanchez BM, Duesberg GS, McEvoy N, Pennycook TJ, Downing C, Crossley A, Nicolosi V, Coleman JN. Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. Nat Mater 2014;13:624–30.
[40] Zhao W, Wu F, Wu H, Chen G. Preparation of colloidal dispersions of graphene sheets in organic solvents by using ball milling. J Nanomater 2010;2010:528235.
[41] Brodie BC. On the atomic weight of graphite. Philos Trans R Soc London 1859;149:249–59.
[42] Staudenmaier L. Verfahren zur darstellung der graphitsure. Ber Dtsch Chem Ges 1898;31:1481–7.
[43] Hummers Jr WS, Offeman RE. Preparation of graphitic oxide. J Am Chem Soc 1958;80:1339.
[44] Gudarzi MM, Moghadam MHM, Sharif F. Spontaneous exfoliation of graphite oxide in polar aprotic solvents as the route to produce graphene oxide organic solvents liquid crystals. Carbon 2013;64:403–15.
[45] He H, Riedl T, Lerf A, Klinowski J. Solid-state NMR studies of the structure of graphite oxide. J Phys Chem 1996;100:19954–8.

[46] Lerf A, He H, Riedl T, Forster M, Klinowski J. ^{13}C and ^{1}H MAS NMR studies of graphite oxide and its chemically modified derivatives. Solid State Ion 1997; 101–103:857–62.
[47] Lerf A, He H, Forster M, Klinowski J. Structure of graphite oxide revisited. J Phys Chem B 1998;102:4477–82.
[48] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. Chem Soc Rev 2010;39:228–40.
[49] Nasrollahzadeh M, Babaei F, Fakhri P, Jaleh B. Synthesis, characterization, structural, optical properties and catalytic activity of reduced graphene oxide/copper nanocomposites. RSC Adv 2015;5:10782–9.
[50] Hontoria-Lucas C, López-Peinado AJ, López-González J de D, Rojas-Cervantes ML, Martín-Aranda RM. Study of oxygen-containing groups in a series of graphite oxides: physical and chemical characterization. Carbon 1995;33:1585–92.
[51] Paredes JI, Villar-Rodil S, Martínez-Alonso A, Tascón JMD. Graphene oxide dispersions in organic solvents. Langmuir 2008;24:10560–4.
[52] Ogino I, Yokoyama Y, Iwamura S, Mukai SR. Exfoliation of graphite oxide in water without sonication: bridging length scales from nanosheets to macroscopic materials. Chem Mater 2014;26:3334–9.
[53] Park S, Ruoff RS. Chemical methods for the production of graphenes. Nat Nanotechnol 2009;4:217–24.
[54] Liao KH, Lin YS, Macosko CW, Haynes CL. Cytotoxicity of graphene oxide and graphene in human erythrocytes and skin fibroblasts. ACS Appl Mater Interfaces 2011;3:2607–15.
[55] Zheng Q, Shi L, Ma PC, Xue Q, Li J, Tang Z, Yang J. Structure control of ultra-large graphene oxide sheets by the Langmuir–Blodgett method. RSC Adv 2013;3: 4680–91.
[56] Botas C, Pérez-Mas AM, Álvarez P, Santamaría R, Granda M, Blanco C, Menéndez R. Optimization of the size and yield of graphene oxide sheets in the exfoliation step. Carbon 2013;63:576–8.
[57] Xu Z, Gao C. Aqueous liquid crystals of graphene oxide. ACS Nano 2011;5:2908–15.
[58] Li P, Wong M, Zhang X, Yao H, Ishige R, Takahara A, Miyamoto M, Nishimura R, Sue HJ. Tunable lyotropic photonic liquid crystal based on graphene oxide. ACS Photonics 2014;1:79–86.
[59] Whitby RLD, Korobeinyk A, Gun'ko VM, Busquets R, Cundy AB, László K, Skubiszewska-Zięba J, Leboda R, Tombacz E, Toth IY, Kovacs K, Mikhalovsky SV. pH-driven physicochemical conformational changes of single-layer graphene oxide. Chem Commun 2011;47:9645–7.
[60] Wu L, Liu L, Gao B, Muoz-Carpena R, Zhang M, Chen H, Zhou Z, Wang H. Aggregation kinetics of graphene oxides in aqueous solutions: experiments, mechanisms, and modeling. Langmuir 2013;29:15174–81.
[61] Ryu S, Lee B, Hong S, Jin S, Park S, Hong SH, Lee H. Salting-out as a scalable, in-series purification method of graphene oxides from microsheets to quantum dots. Carbon 2013;63:45–53.
[62] Wang X, Bai H, Shi G. Size fractionation of graphene oxide sheets by pH-assisted selective sedimentation. J Am Chem Soc 2011;133:6338–42.
[63] Shih CJ, Lin S, Sharma R, Strano MS, Blankschtein D. Understanding the pH-dependent behavior of graphene oxide aqueous solutions: a comparative experimental and molecular dynamics simulation study. Langmuir 2012;28:235–41.
[64] Sun X, Luo D, Liu J, Evans DG. Monodisperse chemically modified graphene obtained by density gradient ultracentrifugal rate separation. ACS Nano 2010;4:3381–9.
[65] Whitby RLD. Chemical control of graphene architecture: tailoring shape and properties. ACS Nano 2014;8:9733–54.
[66] Schniepp HC, Li JL, McAllister MJ, Sai H, Herrera-Alonso M, Adamson DH, Prud'homme RK, Car R, Saville DA, Aksay IA. Functionalized single graphene sheets derived from splitting graphite oxide. J Phys Chem B 2006;110:8535–9.
[67] Mattevi C, Eda G, Agnoli S, Miller S, Mkhoyan KA, Celik O, Mastrogiovanni D, Granozzi G, Garfunkel E, Chhowalla M. Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films. Adv Funct Mater 2009;19:2577–83.
[68] Paredes JI, Villar-Rodil S, Solís-Fernández P, Martínez-Alonso A, Tascón JMD. Atomic force and scanning tunneling microscopy imaging of graphene nanosheets derived from graphite oxide. Langmuir 2009;25:5957–68.
[69] Jyothirmayee Aravind SS, Ramaprabhu S. Surfactant free graphene nanosheets based nanofluids by in-situ reduction of alkaline graphite oxide suspensions. J Appl Phys 2011;110:124326.
[70] Villar-Rodil S, Paredes JI, Martínez-Alonso A, Tascón JMD. Preparation of graphene dispersions and graphene–polymer composites in organic media. J Mater Chem 2009;19:3591–3.
[71] Luo J, Jang HD, Sun T, Xiao L, He Z, Katsoulidis AP, Kanatzidis MG, Gibson JM, Huang J. Compression and aggregation-resistant particles of crumpled soft sheets. ACS Nano 2011;5:8943–9.
[72] Luo J, Kim J, Huang J. Material processing of chemically modified graphene: some challenges and solutions. Acc Chem Res 2013;46:2225–34.
[73] Novoselov KS, Fal'ko VI, Colombo L, Gellert PR, Schwab MG, Kim K. A roadmap for graphene. Nature 2012;490:192–200.
[74] Ferrari AC, Bonaccorso F, Fal'ko V, Novoselov KS, Roche S, Bøggild P, Borini S, Koppens FHL, Palermo V, Pugno N, Garrido JA, Sordan R, Bianco A, Ballerini L, Prato M, Lidorikis E, Kivioja J, Marinelli C, Ryhänen T, Morpurgo A, Coleman JN, Nicolosi V, Colombo L, Fert A, Garcia-Hernandez M, Bachtold A, Schneider GF, Guinea F, Dekker C, Barbone M, Sun Z, Galiotis C, Grigorenko AN, Konstantatos G, Kis A, Katsnelson M, Vandersypen L, Loiseau A, Morandi V, Neumaier D, Treossi E, Pellegrini V, Polini M, Tredicucci A, Williams GM, Hee Hong B, Ahn JH, Min Kim J, Zirath H, van Wees BJ, van der Zant H, Occhipinti L, Di Matteo A, Kinloch IA, Seyller T, Quesnel E, Feng X, Teo K, Rupesinghe N, Hakonen P, Neil SRT, Tannock Q, Löfwander T, Kinaret J. Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. Nanoscale 2015;7:4598–810.
[75] Maxwell JC. Treatise on electricity and magnetism. Oxford: Clarendon Press; 1873.
[76] Wei Y, Huaqing X, Dan B. Enhanced thermal conductivities of nanofluids containing graphene oxide nanosheets. Nanotechnology 2010;21:055705.
[77] Yu W, Xie H, Chen W. Experimental investigation on thermal conductivity of nanofluids containing graphene oxide nanosheets. J Appl Phys 2010;107:094317.
[78] Mahanta NK Abramson AR. Thermal conductivity of graphene and graphene oxide nanoplatelets. Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm), 2012 13th IEEE Intersociety Conference on, (2012 May 30-June 1). San Diego, USA: Piscataway: IEEE; 2012 1–6. http://dx.doi.org/10.1109/ITHERM.2012.6231405.
[79] Zhang H, Fonseca AF, Cho K. Tailoring thermal transport property of graphene through oxygen functionalization. J Phys Chem C 2014;118:1436–42.
[80] Baby TT, Ramaprabhu S. Investigation of thermal and electrical conductivity of graphene based nanofluids. J Appl Phys 2010;108:124308.
[81] Baby TT, Ramaprabhu S. Enhanced convective heat transfer using graphene dispersed nanofluids. Nanoscale Res Lett 2011;6:289.
[82] Yu W, Xie H, Wang X, Wang X. Significant thermal conductivity enhancement for nanofluids containing graphene nanosheets. Phys Lett A 2011;375:1323–8.
[83] Lin J, Wang L, Chen G. Modification of graphene platelets and their tribological properties as a lubricant additive. Tribol Lett 2011;41:209–15.
[84] Wei Z, Ming Z, Hongwei Z, Yu T, Kunlin W, Jinquan W, Fei J, Xiao L, Zhen L, Peng Z, Dehai W. Tribological properties of oleic acid-modified graphene as lubricant oil additives. J Phys D Appl Phys 2011;44:205303.
[85] Choudhary S, Mungse HP, Khatri OP. Dispersion of alkylated graphene in organic solvents and its potential for lubrication applications. J Mater Chem 2012;22: 21032–9.
[86] Eswaraiah V, Sankaranarayanan V, Ramaprabhu S. Graphene-based engine oil nanofluids for tribological applications. ACS Appl Mater Interfaces 2011;3:4221–7.
[87] Song HJ, Li N. Frictional behavior of oxide graphene nanosheets as water-base lubricant additive. Appl Phys A Mater Sci Process 2011;105:827–32.
[88] Stankovich S, Piner RD, Nguyen ST, Ruoff RS. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. Carbon 2006;44:3342–7.
[89] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, Piner RD, Nguyen ST, Ruoff RS. Graphene-based composite materials. Nature 2006;442: 282–6.
[90] Salavagione HJ, Martínez G, Gómez MA. Synthesis of poly(vinyl alcohol)/reduced graphite oxide nanocomposites with improved thermal and electrical properties. J Mater Chem 2009;19:5027–32.
[91] Kim H, Macosko CW. Processing–property relationships of polycarbonate/graphene composites. Polymer 2009;50:3797–809.
[92] Kim H, Miura Y, Macosko CW. Graphene/polyurethane nanocomposites for improved gas barrier and electrical conductivity. Chem Mater 2010;22:3441–50.
[93] Ramanathan T, Abdala AA, Stankovich S, Dikin DA, Herrera Alonso M, Piner RD, Adamson DH, Schniepp HC, Chen X, Ruoff RS, Nguyen ST, Aksay IA, Prud'Homme RK, Brinson LC. Functionalized graphene sheets for polymer nanocomposites. Nat Nanotechnol 2008;3:327–31.
[94] Liao KH, Aoyama S, Abdala AA, Macosko C. Does graphene change T_g of nanocomposites? Macromolecules 2014;47:8311–9.
[95] Wang X, Hu Y, Song L, Yang H, Xing W, Lu H. In situ polymerization of graphene nanosheets and polyurethane with enhanced mechanical and thermal properties. J Mater Chem 2011;21:4222–7.
[96] Gonçalves G, Marques PAAP, Barros-Timmons A, Bdkin I, Singh MK, Emami N, Grácio J. Graphene oxide modified with PMMA via ATRP as a reinforcement filler. J Mater Chem 2010;20:9927–34.
[97] Wang Y, Shi Z, Yin J. Kevlar oligomer functionalized graphene for polymer composites. Polymer 2011;52:3661–70.
[98] Kalaitzidou K, Fukushima H, Drzal LT. A new compounding method for exfoliated graphitepolypropylene nanocomposites with enhanced flexural properties and lower percolation threshold. Compos Sci Technol 2007;67:2045–51.
[99] Araby S, Zaman I, Meng Q, Kawashima N, Michelmore A, Kuan HC, Majewski P, Ma J, Zhang L. Melt compounding with graphene to develop functional, high-performance elastomers. Nanotechnology 2013;24:165601.
[100] Ryu SH, Shanmugharaj A. Influence of hexamethylene diamine functionalized graphene oxide on the melt crystallization and properties of polypropylene nanocomposites. Mater Chem Phys 2014;146:478–86.
[101] Shen B, Zhai W, Tao M, Lu D, Zheng W. Enhanced interfacial interaction between polycarbonate and thermally reduced graphene induced by melt blending. Compos Sci Technol 2013;86:109–16.
[102] Vallés C, Abdelkader AM, Young RJ, Kinloch IA. Few layer graphene–polypropylene nanocomposites: the role of flake diameter. Faraday Discuss 2014;173:379–90.
[103] Hu W, Peng C, Luo W, Lv M, Li X, Li D, Huang Q, Fan C. Graphene-based antibacterial paper. ACS Nano 2010;4:4317–23.
[104] Wei Z, Wang D, Kim S, Kim SY, Hu Y, Yakes MK, Laracuente AR, Dai Z, Marder SR, Berger C, King WP, de Heer WA, Sheehan PE, Riedo E. Nanoscale tunable reduction of graphene oxide for graphene electronics. Science 2010;328:1373–6.
[105] Eda G, Fanchini G, Chhowalla M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. Nat Nanotechnol 2008;3:270–4.
[106] Yin Z, Sun S, Salim T, Wu S, Huang X, He Q, Lam YM, Zhang H. Organic photovoltaic devices using highly flexible reduced graphene oxide films as transparent electrodes. ACS Nano 2010;4:5263–8.
[107] Hwang H, Joo P, Kang MS, Ahn G, Han JT, Kim BS, Cho JH. Highly tunable charge transport in layer-by-layer assembled graphene transistors. ACS Nano 2012;6: 2432–40.
[108] Bae SY, Jeon IY, Yang J, Park N, Shin HS, Park S, Ruoff RS, Dai L, Baek JB. Large-area graphene films by simple solution casting of edge-selectively functionalized graphite. ACS Nano 2011;5:4974–80.

[109] Pu NW, Wang CA, Liu YM, Sung Y, Wang DS, Ger MD. Dispersion of graphene in aqueous solutions with different types of surfactants and the production of graphene films by spray or drop coating. J Taiwan Inst Chem Eng 2012;43:140–6.
[110] Fernández-Merino MJ, Paredes JI, Villar-Rodil S, Guardia L, Solís-Fernández P, Salinas-Torres D, Cazorla-Amorós D, Morallón E, Martínez-Alonso A, Tascón JMD. Investigating the influence of surfactants on the stabilization of aqueous reduced graphene oxide dispersions and the characteristics of their composite films. Carbon 2012;50:3184–94.
[111] Xi Q, Chen X, Evans DG, Yang W. Gold nanoparticle-embedded porous graphene thin films fabricated via layer-by-layer self-assembly and subsequent thermal annealing for electrochemical sensing. Langmuir 2012;28:9885–92.
[112] Zhao J, Pei S, Ren W, Gao L, Cheng HM. Efficient preparation of large-area graphene oxide sheets for transparent conductive films. ACS Nano 2010;4:5245–52.
[113] Zhu J, Chen M, He Q, Shao L, Wei S, Guo Z. An overview of the engineered graphene nanostructures and nanocomposites. RSC Adv 2013;3:22790–824.
[114] Xu Y, Bai H, Lu G, Li C, Shi G. Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets. J Am Chem Soc 2008;130:5856–7.
[115] Sun P, Zhu M, Wang K, Zhong M, Wei J, Wu D, Xu Z, Zhu H. Selective ion penetration of graphene oxide membranes. ACS Nano 2013;7:428–37.
[116] Wang M, Oh J, Ghosh T, Hong S, Nam G, Hwang T, Nam JD. An interleaved porous laminate composed of reduced graphene oxide sheets and carbon black spacers by in situ electrophoretic deposition. RSC Adv 2014;4:3284–92.
[117] Zou J, Kim F. Diffusion driven layer-by-layer assembly of graphene oxide nanosheets into porous three-dimensional macrostructures. Nat Commun 2014;5:5254.
[118] Chen JJ, Meng J, Zhou YB, Wu HC, Bie YQ, Liao ZM, Yu DP. Layer-by-layer assembly of vertically conducting graphene devices. Nat Commun 2013;4:1921.
[119] Wang D, Yang J, Li X, Geng D, Li R, Cai M, Sham TK, Sun X. Layer by layer assembly of sandwiched graphene/SnO_2 nanorod/carbon nanostructures with ultrahigh lithium ion storage properties. Energy Environ Sci 2013;6:2900–6.
[120] Ji Q, Honma I, Paek SM, Akada M, Hill JP, Vinu A, Ariga K. Layer-by-layer films of graphene and ionic liquids for highly selective gas sensing. Angew Chem Int Ed 2010;49:9737–9.
[121] Yu D, Dai L. Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. J Phys Chem Lett 2010;1:467–70.
[122] Lee JK, Smith KB, Hayner CM, Kung HH. Silicon nanoparticles–graphene paper composites for Li ion battery anodes. Chem Commun 2010;46:2025–7.
[123] Goh MS, Pumera M. Graphene-based electrochemical sensor for detection of 2,4,6-trinitrotoluene (TNT) in seawater: the comparison of single-, few-, and multilayer graphene nanoribbons and graphite microparticles. Anal Bioanal Chem 2011;399:127–31.
[124] Zhao G, Li J, Ren X, Chen C, Wang X. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. Environ Sci Technol 2011;45:10454–62.
[125] Li C, Shi G. Functional gels based on chemically modified graphenes. Adv Mater 2014;26:3992–4012.
[126] Zhang L, Shi G. Preparation of highly conductive graphene hydrogels for fabricating supercapacitors with high rate capability. J Phys Chem C 2011;115:17206–12.
[127] Bi H, Xie X, Yin K, Zhou Y, Wan S, He L, Xu F, Banhart F, Sun L, Ruoff RS. Spongy graphene as a highly efficient and recyclable sorbent for oils and organic solvents. Adv Funct Mater 2012;22:4421–5.
[128] Xu Y, Wu Q, Sun Y, Bai H, Shi G. Three-dimensional self-assembly of graphene oxide and DNA into multifunctional hydrogels. ACS Nano 2010;4:7358–62.
[129] Bagreev A, Bandosz TJ. H_2S adsorption/oxidation on unmodified activated carbons: importance of prehumidification. Carbon 2001;39:2303–11.
[130] Bai H, Li C, Wang X, Shi G. A pH-sensitive graphene oxide composite hydrogel. Chem Commun 2010;46:2376–8.
[131] Bai H, Li C, Wang X, Shi G. On the gelation of graphene oxide. J Phys Chem C 2011;115:5545–51.
[132] Gun J, Kulkarni SA, Xiu W, Batabyal SK, Sladkevich S, Prikhodchenko PV, Gutkin V, Lev O. Graphene oxide organogel electrolyte for quasi solid dye sensitized solar cells. Electrochem Commun 2012;19:108–10.
[133] Xu Y, Sheng K, Li C, Shi G. Self-assembled graphene hydrogel via a one-step hydrothermal process. ACS Nano 2010;4:4324–30.
[134] Sun Y, Wu Q, Shi G. Supercapacitors based on self-assembled graphene organogel. Phys Chem Chem Phys 2011;13:17249–54.
[135] Dua V, Surwade S, Ammu S, Agnihotra S, Jain S, Roberts K, Park S, Ruoff R, Manohar S. All-organic vapor sensor using inkjet-printed reduced graphene oxide. Angew Chem Int Ed 2010;49:2154–7.
[136] Torrisi F, Hasan T, Wu W, Sun Z, Lombardo A, Kulmala TS, Hsieh GW, Jung S, Bonaccorso F, Paul PJ, Chu D, Ferrari AC. Inkjet-printed graphene electronics. ACS Nano 2012;6:2992–3006.
[137] Shin KY, Hong JY, Jang J. Micropatterning of graphene sheets by inkjet printing and its wideband dipole-antenna application. Adv Mater 2011;23:2113–8.
[138] Le LT, Ervin MH, Qiu H, Fuchs BE, Lee WY. Graphene supercapacitor electrodes fabricated by inkjet printing and thermal reduction of graphene oxide. Electrochem Commun 2011;13:355–8.
[139] de Gans BJ, Duineveld PC, Schubert US. Inkjet printing of polymers: state of the art and future developments. Adv Mater 2004;16:203–13.
[140] Jang D, Kim D, Moon J. Influence of fluid physical properties on ink-jet printability. Langmuir 2009;25:2629–35.
[141] Li J, Ye F, Vaziri S, Muhammed M, Lemme MC, Östling M. Efficient inkjet printing of graphene. Adv Mater 2013;25:3985–92.
[142] Secor EB, Prabhumirashi PL, Puntambekar K, Geier ML, Hersam MC. Inkjet printing of high conductivity, flexible graphene patterns. J Phys Chem Lett 2013;4:1347–51.
[143] Wang S, Sun H, Ang HM, Tadé MO. Adsorptive remediation of environmental pollutants using novel graphene-based nanomaterials. Chem Eng J 2013;226:336–47.
[144] Kemp KC, Seema H, Saleh M, Le NH, Mahesh K, Chandra V, Kim KS. Environmental applications using graphene composites: water remediation and gas adsorption. Nanoscale 2013;5:3149–71.
[145] Yang ST, Chang Y, Wang H, Liu G, Chen S, Wang Y, Liu Y, Cao A. Folding/aggregation of graphene oxide and its application in Cu^{2+} removal. J Colloid Interface Sci 2010;351:122–7.
[146] Lee YC, Yang JW. Self-assembled flower-like TiO_2 on exfoliated graphite oxide for heavy metal removal. J Ind Eng Chem 2012;18:1178–85.
[147] Zhao G, Ren X, Gao X, Tan X, Li J, Chen C, Huang Y, Wang X. Removal of Pb(II) ions from aqueous solutions on few-layered graphene oxide nanosheets. Dalton Trans 2011;40:10945–52.
[148] Madadrang CJ, Kim HY, Gao G, Wang N, Zhu J, Feng H, Gorring M, Kasner ML, Hou S. Adsorption behavior of EDTA–graphene oxide for Pb(II) removal. ACS Appl Mater Interfaces 2012;4:1186–93.
[149] Huang ZH, Zheng X, Lv W, Wang M, Yang QH, Kang F. Adsorption of lead(II) ions from aqueous solution on low-temperature exfoliated graphene nanosheets. Langmuir 2011;27:7558–62.
[150] Gao W, Majumder M, Alemany LB, Narayanan TN, Ibarra MA, Pradhan BK, Ajayan PM. Engineered graphite oxide materials for application in water purification. ACS Appl Mater Interfaces 2011;3:1821–6.
[151] Chandra V, Kim KS. Highly selective adsorption of Hg^{2+} by a polypyrrole-reduced graphene oxide composite. Chem Commun 2011;47:3942–4.
[152] Ren Y, Yan N, Wen Q, Fan Z, Wei T, Zhang M, Ma J. Graphene/δ-MnO_2 composite as adsorbent for the removal of nickel ions from wastewater. Chem Eng J 2011;175:1–7.
[153] Mishra AK, Ramaprabhu S. Functionalized graphene sheets for arsenic removal and desalination of sea water. Desalination 2011;282:39–45.
[154] Chandra V, Park J, Chun Y, Lee JW, Hwang IC, Kim KS. Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. ACS Nano 2010;4:3979–86.
[155] Wu XL, Wang L, Chen CL, Xu AW, Wang XK. Water-dispersible magnetite–graphene–LDH composites for efficient arsenate removal. J Mater Chem 2011;21:17353–9.
[156] Jabeen H, Chandra V, Jung S, Lee JW, Kim KS, Kim SB. Enhanced Cr(VI) removal using iron nanoparticle decorated graphene. Nanoscale 2011;3:3583–5.
[157] Yang ST, Chen S, Chang Y, Cao A, Liu Y, Wang H. Removal of methylene blue from aqueous solution by graphene oxide. J Colloid Interface Sci 2011;359:24–9.
[158] Zhang W, Zhou C, Zhou W, Lei A, Zhang Q, Wan Q, Zou B. Fast and considerable adsorption of methylene blue dye onto graphene oxide. Bull Environ Contam Toxicol 2011;87:86–90.
[159] Bradder P, Ling SK, Wang S, Liu S. Dye adsorption on layered graphite oxide. J Chem Eng Data 2011;56:138–41.
[160] Georgakilas V, Otyepka M, Bourlinos AB, Chandra V, Kim N, Kemp KC, Hobza P, Zboril R, Kim KS. Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications. Chem Rev 2012;112:6156–214.
[161] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of carbon nanotubes. Chem Rev 2006;106:1105–36.
[162] Zhao YL, Stoddart JF. Noncovalent functionalization of single-walled carbon nanotubes. Acc Chem Res 2009;42:1161–71.
[163] Grimme S. Do special noncovalent ππ stacking interactions really exist? Angew Chem Int Ed 2008;47:3430–4.
[164] Su YH, Wu YK, Tu SL, Chang SJ. Electrostatic studies of π–π interaction for benzene stacking on a graphene layer. Appl Phys Lett 2011;99:163102.
[165] Björk J, Hanke F, Palma CA, Samori P, Cecchini M, Persson M. Adsorption of aromatic and anti-aromatic systems on graphene through stacking. J Phys Chem Lett 2010;1:3407–12.
[166] Wang W, Zhang Y, Wang YB. Noncovalent π-π interaction between graphene and aromatic molecule: structure, energy, and nature. J Chem Phys 2014;140:094302.
[167] Kocman M, Pykal M, Jurečka P. Electric quadrupole moment of graphene and its effect on intermolecular interactions. Phys Chem Chem Phys 2014;16:3144–52.
[168] Zu SZ, Zhou D, Han BH. Supramolecular surface modification and dispersion of graphene in water and organic solvents. J Nanosci Nanotechnol 2013;13:946–53.
[169] Parviz D, Das S, Ahmed HST, Irin F, Bhattacharia S, Green MJ. Dispersions of non-covalently functionalized graphene with minimal stabilizer. ACS Nano 2012;6:8857–67.
[170] Zhang M, Gao B, Li Y, Zhang X, Hardin IR. Graphene-coated pyrogenic carbon as an anode material for lithium battery. Chem Eng J 2013;229:399–403.
[171] Gao T, Ye Q, Pei X, Xia Y, Zhou F. Grafting polymer brushes on graphene oxide for controlling surface charge states and templated synthesis of metal nanoparticles. J Appl Polym Sci 2013;127:3074–83.
[172] Lee DW, Kim T, Lee M. An amphiphilic pyrene sheet for selective functionalization of graphene. Chem Commun 2011;47:8259–61.
[173] Liu J, Tao L, Yang W, Li D, Boyer C, Wuhrer R, Braet F, Davis TP. Synthesis, characterization, and multilayer assembly of pH sensitive graphene–polymer nanocomposites. Langmuir 2010;26:10068–75.
[174] Ihiawakrim D, Ersen O, Melin F, Hellwig P, Janowska I, Begin D, Baaziz W, Begin-Colin S, Cuong PH, Baati R. A single-stage functionalization and exfoliation method for the production of graphene in water: stepwise construction of 2D-nanostructured composites with iron oxide nanoparticles. Nanoscale 2013;5:9073–80.
[175] Lu CH, Li J, Zhang XL, Zheng AX, Yang HH, Chen X, Chen GN. General approach for monitoring peptide–protein interactions based on graphene–peptide complex. Anal Chem 2011;83:7276–82.
[176] Patil AJ, Vickery JL, Scott TB, Mann S. Aqueous stabilization and self-assembly of graphene sheets into layered bio-nanocomposites using DNA. Adv Mater 2009;21:3159–64.

[177] Wan L, Wang B, Wang S, Wang X, Guo Z, Xiong H, Dong B, Zhao L, Lu H, Xu Z, Zhang X, Li T, Zhou W. Water-soluble polyaniline/graphene prepared by in situ polymerization in graphene dispersions and use as counter-electrode materials for dye-sensitized solar cells. React Funct Polym 2014;79:47–53.
[178] Bai H, Xu Y, Zhao L, Li C, Shi G. Non-covalent functionalization of graphene sheets by sulfonated polyaniline. Chem Commun 2009:1667–9.
[179] Jo K, Lee T, Choi HJ, Park JH, Lee DJ, Lee DW, Kim BS. Stable aqueous dispersion of reduced graphene nanosheets via non-covalent functionalization with conducting polymers and application in transparent electrodes. Langmuir 2011;27:2014–8.
[180] Wang J, Chen Z, Chen B. Adsorption of polycyclic aromatic hydrocarbons by graphene and graphene oxide nanosheets. Environ Sci Technol 2014;48:4817–25.
[181] Lazar P, Otyepková E, Banáš P, Fargašová A, Šafářová K, Lapčík L, Pechoušek J, Zbořil R, Otyepka M. The nature of high surface energy sites in graphene and graphite. Carbon 2014;73:448–53.
[182] Wang H, Bi SG, Ye YS, Xue Y, Xie XL, Mai YW. An effective non-covalent grafting approach to functionalize individually dispersed reduced graphene oxide sheets with high grafting density, solubility and electrical conductivity. Nanoscale 2015;7:3548–57.
[183] Schlierf A, Yang H, Gebremedhn E, Treossi E, Ortolani L, Chen L, Minoia A, Morandi V, Samori P, Casiraghi C, Beljonne D, Palermo V. Nanoscale insight into the exfoliation mechanism of graphene with organic dyes: effect of charge, dipole and molecular structure. Nanoscale 2013;5:4205–16.
[184] Wang H, Chen Z, Xin L, Cui J, Zhao S, Yan Y. Synthesis of pyrene-capped polystyrene by free radical polymerization and its application in direct exfoliation of graphite into graphene nanosheets. J Polym Sci A Polym Chem 2015;53:2175–85.
[185] Zheng X, Xu Q, Li J, Li L, Wei J. High-throughput, direct exfoliation of graphite to graphene via a cooperation of supercritical CO_2 and pyrene-polymers. RSC Adv 2012;2:10632–8.
[186] Ling D, Yang X, Pulford CTR, The Goodyear Tire & Rubber Company, Akron OH. Tire with component comprised of rubber composition containing silica and graphene platelet reinforcement; November 30, 2012 US 9090756 B2.
[187] Liu J, Yang W, Tao L, Li D, Boyer C, Davis TP. Thermosensitive graphene nanocomposites formed using pyrene-terminal polymers made by RAFT polymerization. J Polym Sci A Polym Chem 2010;48:425–33.
[188] Popescu MT, Tasis D, Tsitsilianis C. Ionizable star copolymer-assisted graphene phase transfer between immiscible liquids: organic solvent/water/ionic liquid. ACS Macro Lett 2014;3:981–4.
[189] Rajesh C, Majumder C, Mizuseki H, Kawazoe Y. A theoretical study on the interaction of aromatic amino acids with graphene and single walled carbon nanotube. J Chem Phys 2009;130:124911.
[190] Hughes ZE, Walsh TR. What makes a good graphene-binding peptide? Adsorption of amino acids and peptides at aqueous graphene interfaces. J Mater Chem B 2015;3:3211–21.
[191] Sriprachuabwong C, Karuwan C, Wisitsorrat A, Phokharatkul D, Lomas T, Sritongkham P, Tuantranont A. Inkjet-printed graphene-PEDOT: PSS modified screen printed carbon electrode for biochemical sensing. J Mater Chem 2012;22:5478–85.
[192] Ayán-Varela M, Paredes JI, Guardia L, Villar-Rodil S, Munuera JM, Díaz-Gonzlez M, Fernández-Sánchez C, Martínez-Alonso A, Tascón JMD. Achieving extremely concentrated aqueous dispersions of graphene flakes and catalytically efficient graphene–metal nanoparticle hybrids with flavin mononucleotide as a high-performance stabilizer. ACS Appl Mater Interfaces 2015;7:10293–307.
[193] Akca S, Foroughi A, Frochtzwajg D, Postma HWC. Competing interactions in DNA assembly on graphene. PLoS One 2011;6, e18442.
[194] Park JS, Na HK, Min DH, Kim DE. Desorption of single-stranded nucleic acids from graphene oxide by disruption of hydrogen bonding. Analyst 2013;138:1745–9.
[195] Dougherty DA. Cation–π interactions in chemistry and biology: a new view of benzene, Phe, Tyr, and Trp. Science 1996;271:163–8.
[196] Kim D, Hu S, Tarakeshwar P, Kim KS, Lisy JM. Cation–π interactions: a theoretical investigation of the interaction of metallic and organic cations with alkenes, arenes, and heteroarenes. J Phys Chem A 2003;107:1228–38.
[197] Kim KS, Lee JY, Lee SJ, Ha TK, Kim DH. On binding forces between aromatic ring and quaternary ammonium compounds. J Am Chem Soc 1994;116:7399–400.
[198] Lee JY, Lee SJ, Choi HS, Cho SJ, Kim KS, Ha TK. *Ab-initio* study of the complexation of benzene with ammonium cations. Chem Phys Lett 1995;232:67–71.
[199] Jeong SY, Kim SH, Han JT, Jeong HJ, Jeong SY, Lee GW. Highly concentrated and conductive reduced graphene oxide nanosheets by monovalent cation–π interaction: toward printed electronics. Adv Funct Mater 2012;22:3307–14.
[200] Geronimo I, Singh NJ, Kim KS. Nature of anion-templated π^+-π^+ interactions. Phys Chem Chem Phys 2011;13:11841–5.
[201] Yang YK, He CE, Peng RG, Baji A, Du XS, Huang YL, Xie XL, Mai YW. Non-covalently modified graphene sheets by imidazolium ionic liquids for multifunctional polymer nanocomposites. J Mater Chem 2012;22:5666–75.
[202] Ghatee MH, Moosavi F. Physisorption of hydrophobic and hydrophilic 1-alkyl-3-methylimidazolium ionic liquids on the graphenes. J Phys Chem C 2011;115:5626–36.
[203] Gao H, Zhang S, Lu F, Jia H, Zheng L. Aqueous dispersion of graphene sheets stabilized by ionic liquid-based polyether. Colloid Polym Sci 2012;290:1785–91.
[204] Lonkar SP, Bobenrieth A, De Winter J, Gerbaux P, Raquez JM, Dubois P. A supramolecular approach toward organo-dispersible graphene and its straightforward polymer nanocomposites. J Mater Chem 2012;22:18124–6.
[205] Hsieh AG, Punckt C, Korkut S, Aksay IA. Adsorption of sodium dodecyl sulfate on functionalized graphene measured by conductometric titration. J Phys Chem B 2013;117:7950–8.
[206] Hsieh AG, Korkut S, Punckt C, Aksay IA. Dispersion stability of functionalized graphene in aqueous sodium dodecyl sulfate solutions. Langmuir 2013;29:14831–8.
[207] Guardia L, Fernández-Merino MJ, Paredes JI, Solís-Fernández P, Villar-Rodil S, Martínez-Alonso A, Tascón JMD. High-throughput production of pristine graphene in an aqueous dispersion assisted by non-ionic surfactants. Carbon 2011;49:1653–62.
[208] Li S, Guo J, Patel RA, Dadlani AL, Leblanc RM. Interaction between graphene oxide and pluronic f127 at the air–water interface. Langmuir 2013;29:5742–8.
[209] Yan Y, Piao L, Kim SH, Li W, Zhou H. Effect of pluronic block copolymers on aqueous dispersions of graphene oxide. RSC Adv 2015;5:40199–204.
[210] Wang H, Xia B, Yan Y, Li N, Wang JY, Wang X. Water-soluble polymer exfoliated graphene: as catalyst support and sensor. J Phys Chem B 2013;117:5606–13.
[211] Cesareo G, Parrini MR, Rizzi LG, Directa Plus S.P.A, Italy. Concentrated water dispersion of graphene and method for the preparation thereof. WO/2014/135455; Feb 28 2014.
[212] Wajid AS, Das S, Irin F, Ahmed HT, Shelburne JL, Parviz D, Fullerton RJ, Jankowski AF, Hedden RC, Green MJ. Polymer-stabilized graphene dispersions at high concentrations in organic solvents for composite production. Carbon 2012;50:526–34.
[213] Bourlinos AB, Georgakilas V, Zboril R, Steriotis TA, Stubos AK, Trapalis C. Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone for the production of water-soluble graphenes. Solid State Commun 2009;149:2172–6.
[214] Yoon S, In I. Role of poly(N-vinyl-2-pyrrolidone) as stabilizer for dispersion of graphene via hydrophobic interaction. J Mater Sci 2011;46:1316–21.
[215] Ou E, Xie Y, Peng C, Song Y, Peng H, Xiong Y, Xu W. High concentration and stable few-layer graphene dispersions prepared by the exfoliation of graphite in different organic solvents. RSC Adv 2013;3:9490–9.
[216] Shan C, Wang L, Han D, Li F, Zhang Q, Zhang X, Niu L. Polyethyleneimine-functionalized graphene and its layer-by-layer assembly with prussian blue. Thin Solid Films 2013;534:572–6.
[217] Wang G, Shen X, Wang B, Yao J, Park J. Synthesis and characterisation of hydrophilic and organophilic graphene nanosheets. Carbon 2009;47:1359–64.
[218] Pinto AM, Martins J, Moreira JA, Mendes AM, Magalhães FD. Dispersion of graphene nanoplatelets in poly(vinyl acetate) latex and effect on adhesive bond strength. Polym Int 2013;62:928–35.
[219] Ager D, Vasantha VA, Crombez R, Texter J. Aqueous graphene dispersions—optical properties and stimuli-responsive phase transfer. ACS Nano 2014;8:11191–205.
[220] Kou L, Gao C. Making silica nanoparticle-covered graphene oxide nanohybrids as general building blocks for large-area superhydrophilic coatings. Nanoscale 2011;3:519–28.
[221] Achari A, Datta KKR, De M, Dravid VP, Eswaramoorthy M. Amphiphilic aminoclay-RGO hybrids: a simple strategy to disperse a high concentration of RGO in water. Nanoscale 2013;5:5316–20.
[222] Wang S, Li H, Zhang L, Li B, Cao X, Zhang G, Zhang S, Wu L. Phase transfer and dispersion of reduced graphene oxide nanosheets using cluster suprasurfactants. Chem Commun 2014;50:9700–3.
[223] de Miguel-Turullois I, Herradón-García B, Mann-Morales EA, Morales-Bergas E. Consejo Superior de Investigaciones Científicas (CSIC) Spain. Exfoliation of graphite with deep eutectic solvents; Aug 12, 2014, WO/2015/044478.
[224] Siddique JA, Attia NF, Geckeler KE. Polymer nanoparticles as a tool for the exfoliation of graphene sheets. Mater Lett 2015;158:186–9.
[225] Xu M, Zhang W, Yang Z, Yu F, Ma Y, Hu N, He D, Liang Q, Su Y, Zhang Y. One-pot liquid-phase exfoliation from graphite to graphene with carbon quantum dots. Nanoscale 2015;7:10527–34.
[226] Criado A, Melchionna M, Marchesan S, Prato M. The covalent functionalization of graphene on substrates. Angew Chem Int Ed 2015;54:10734–50.
[227] Park J, Yan M. Covalent functionalization of graphene with reactive intermediates. Acc Chem Res 2013;46:181–9.
[228] Chua CK, Pumera M. Covalent chemistry on graphene. Chem Soc Rev 2013;42:3222–33.
[229] Jang J, Pham VH, Hur SH, Chung JS. Dispersibility of reduced alkylamine-functionalized graphene oxides in organic solvents. J Colloid Interface Sci 2014;424:62–6.
[230] Karthick R, Brindha M, Selvaraj M, Ramu S. Stable colloidal dispersion of functionalized reduced graphene oxide in aqueous medium for transparent conductive film. J Colloid Interface Sci 2013;406:69–74.
[231] Lomeda JR, Doyle CD, Kosynkin DV, Hwang WF, Tour JM. Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. J Am Chem Soc 2008;130:16201–6.
[232] Dubin S, Gilje S, Wang K, Tung VC, Cha K, Hall AS, Farrar J, Varshneya R, Yang Y, Kaner RB. A one-step, solvothermal reduction method for producing reduced graphene oxide dispersions in organic solvents. ACS Nano 2010;4:3845–52.
[233] Roy S, Soin N, Bajpai R, Misra DS, McLaughlin JA, Roy SS. Graphene oxide for electrochemical sensing applications. J Mater Chem 2011;21:14725–31.
[234] Liu Z, Robinson JT, Sun X, Dai H. PEGylated nanographene oxide for delivery of water-insoluble cancer drugs. J Am Chem Soc 2008;130:10876–7.
[235] Chen B, Liu M, Zhang L, Huang J, Yao J, Zhang Z. Polyethylenimine-functionalized graphene oxide as an efficient gene delivery vector. J Mater Chem 2011;21:7736–41.
[236] Cano M, Khan U, Sainsbury T, O'Neill A, Wang Z, McGovern IT, Maser WK, Benito AM, Coleman JN. Improving the mechanical properties of graphene oxide based materials by covalent attachment of polymer chains. Carbon 2013;52:363–71.
[237] Veca LM, Lu F, Meziani MJ, Cao L, Zhang P, Qi G, Qu L, Shrestha M, Sun YP. Polymer functionalization and solubilization of carbon nanosheets. Chem Commun 2009:2565–7.

[238] Mohanty N, Berry V. Graphene-based single-bacterium resolution biodevice and DNA transistor: interfacing graphene derivatives with nanoscale and microscale biocomponents. Nano Lett 2008;8:4469–76.
[239] Yan JL, Chen GJ, Cao J, Yang W, Xie BH, Yang MB. Functionalized graphene oxide with ethylenediamine and 1,6-hexanediamine. New Carbon Mater 2012;27:370–6.
[240] Xu C, Wang X, Wang J, Hu H, Wan L. Synthesis and photoelectrical properties of β-cyclodextrin functionalized graphene materials with high bio-recognition capability. Chem Phys Lett 2010;498:162–7.
[241] Pham TA, Choi BC, Jeong YT. Facile covalent immobilization of cadmium sulfide quantum dots on graphene oxide nanosheets: preparation, characterization, and optical properties. Nanotechnology 2010;21:465603.
[242] Xu Y, Liu Z, Zhang X, Wang Y, Tian J, Huang Y, Ma Y, Zhang X, Chen Y. A graphene hybrid material covalently functionalized with porphyrin: synthesis and optical limiting property. Adv Mater 2009;21:1275–9.
[243] Zhang X, Huang Y, Wang Y, Ma Y, Liu Z, Chen Y. Synthesis and characterization of a graphene–C_{60} hybrid material. Carbon 2009;47:334–7.
[244] Thomas HR, Marsden AJ, Walker M, Wilson NR, Rourke JP. Sulfur-functionalized graphene oxide by epoxide ring-opening. Angew Chem Int Ed 2014;53:7613–8.
[245] Deng Y, Li Y, Dai J, Lang M, Huang X. Functionalization of graphene oxide towards thermo-sensitive nanocomposites via moderate in situ SET-LRP. J Polym Sci A Polym Chem 2011;49:4747–55.
[246] Collins WR, Schmois E, Swager TM. Graphene oxide as an electrophile for carbon nucleophiles. Chem Commun 2011;47:8790–2.
[247] Hou S, Su S, Kasner ML, Shah P, Patel K, Madarang CJ. Formation of highly stable dispersions of silane-functionalized reduced graphene oxide. Chem Phys Lett 2010;501:68–74.
[248] Wan YJ, Gong LX, Tang LC, Wu LB, Jiang JX. Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide. Composites Part A 2014;64:79–89.
[249] Li GL, Liu G, Li M, Wan D, Neoh KG, Kang ET. Organo- and water-dispersible graphene oxide polymer nanosheets for organic electronic memory and gold nanocomposites. J Phys Chem C 2010;114:12742–8.
[250] Lee SH, Dreyer DR, An J, Velamakanni A, Piner RD, Park S, Zhu Y, Kim SO, Bielawski CW, Ruoff RS. Polymer brushes via controlled, surface-initiated atom transfer radical polymerization (ATRP) from graphene oxide. Macromol Rapid Commun 2010;31:281–8.
[251] Shen J, Hu Y, Li C, Qin C, Ye M. Synthesis of amphiphilic graphene nanoplatelets. Small 2009;5:82–5.
[252] Hsiao MC, Liao SH, Yen MY, Liu PI, Pu NW, Wang CA, Ma CCM. Preparation of covalently functionalized graphene using residual oxygen-containing functional groups. ACS Appl Mater Interfaces 2010;2:3092–9.
[253] Feng Y, Liu H, Luo W, Liu E, Zhao N, Yoshino K, Feng W. Covalent functionalization of graphene by azobenzene with molecular hydrogen bonds for long-term solar thermal storage. Sci Rep 2013;3:3260.
[254] Zhu Y, Higginbotham AL, Tour JM. Covalent functionalization of surfactant-wrapped graphene nanoribbons. Chem Mater 2009;21:5284–91.
[255] Wei G, Yan M, Dong R, Wang D, Zhou X, Chen J, Hao J. Covalent modification of reduced graphene oxide by means of diazonium chemistry and use as a drug-delivery system. Chem Eur J 2012;18:14708–16.
[256] Irin F, Hansen MJ, Bari R, Parviz D, Metzler SD, Bhattacharia SK, Green MJ. Adsorption and removal of graphene dispersants. J Colloid Interface Sci 2015;446:282–9.
[257] Guidelines for the characterization of dispersion stability. ISO/TR 13097; 2013 Published 2013.
[258] Huang X, Yin Z, Wu S, Qi X, He Q, Zhang Q, Yan Q, Boey F, Zhang H. Graphene-based materials: synthesis, characterization, properties, and applications. Small 2011;7:1876–902.
[259] Liu WW, Chai SP, Mohamed AR, Hashim U. Synthesis and characterization of graphene and carbon nanotubes: a review on the past and recent developments. J Ind Eng Chem 2014;20:1171–85.
[260] Dezhi C, Lidong L, Lin G. An environment-friendly preparation of reduced graphene oxide nanosheets via amino acid. Nanotechnology 2011;22:325601.
[261] Khan U, O'Neill A, Lotya M, De S, Coleman JN. High-concentration solvent exfoliation of graphene. Small 2010;6:864–71.
[262] Lotya M, King PJ, Khan U, De S, Coleman JN. High-concentration, surfactant-stabilized graphene dispersions. ACS Nano 2010;4:3155–62.
[263] Su R, Lin SF, Chen DQ, Chen GH. Study on the absorption coefficient of reduced graphene oxide dispersion. J Phys Chem C 2014;118:12520–5.
[264] Nuvoli D, Valentini L, Alzari V, Scognamillo S, Bon SB, Piccinini M, Illescas J, Mariani A. High concentration few-layer graphene sheets obtained by liquid phase exfoliation of graphite in ionic liquid. J Mater Chem 2011;21:3428–31.
[265] Zhang W, He W, Jing X. Preparation of a stable graphene dispersion with high concentration by ultrasound. J Phys Chem B 2010;114:10368–73.
[266] Xu R. Light scattering: a review of particle characterization applications. Particuology 2015;18:11–21.
[267] Catheline A, Ortolani L, Morandi V, Melle-Franco M, Drummond C, Zakri C, Pénicaud A. Solutions of fully exfoliated individual graphene flakes in low boiling point solvents. Soft Matter 2012;8:7882–7.
[268] Lotya M, Rakovich A, Donegan JF, Coleman JN. Measuring the lateral size of liquid-exfoliated nanosheets with dynamic light scattering. Nanotechnology 2013;24:265703.
[269] Liu WW, Wang JN, Wang XX. Charging of unfunctionalized graphene in organic solvents. Nanoscale 2012;4:425–8.
[270] Konkena B, Vasudevan S. Understanding aqueous dispersibility of graphene oxide and reduced graphene oxide through pka measurements. J Phys Chem Lett 2012;3:867–72.
[271] Hunter R. Zeta potential in colloid science: principles and applications. Waltham: Academic Press; 1981.
[272] Schramm L. Emulsions, foams, and suspensions: fundamentals and applications. Hoboken: Wiley; 2005.
[273] Doane TL, Chuang CH, Hill RJ, Burda C. Nanoparticle ζ-potentials. Acc Chem Res 2012;45:317–26.
[274] Li D, Müller MB, Gilje S, Kaner RB, Wallace GG. Processable aqueous dispersions of graphene nanosheets. Nat Nanotechnol 2008;3:101–5.